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CASE STUDIES OF HAZARDOUS WASTE TREATMENT TO REMOVE VOLATILE ORGANICS: VOLUME II

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Case studies are presented for treatment of refinery wastes in a pilot-scale thin-film evaporator, the removal of volatiles from industrial wastewater for two steam strippers, and the removal of semivolatiles from water by steam stripping followed by liquid-phase carbon adsorption. This report provides data on removal efficiency, air emissions, process residuals, treatment costs, and process limitations. Details on sampling and analytical procedures, quality assurance, and process data are contained in the Appendixes (Volume II).

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important environmental and public health implications. The Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving these problems. Its products support the policies, programs, and regulations of the Environmental Protection Agency, the permitting and other responsibilities of State and local governments and the needs of both large and small and businesses in handling their wastes responsibly and economically.

This report presents the results of field assessments of three waste treatment techniques that have the potential for use in control of emissions of volatile organic compounds from hazardous waste facilities by removing those compounds from the waste streams. Those treatment techniques are thin-film evaporation, steam stripping, and steam stripping with carbon adsorption. The report is intended for use by government agencies which are considering ways to reduce emissions from hazardous waste facilities and by facility operators and managers who wish to do the same. For additional information, please contact the Alternative Technologies Division of the Hazardous Waste Engineering Research Laboratory.

Thomas R. Hauser, Director
Hazardous Waste Engineering Research Laboratory

ABSTRACT

Three treatment processes were investigated for the removal of volatile organic (VO) compounds from hazardous waste: thin-film evaporation, steam stripping, and steam stripping with carbon adsorption. The data collected included the VO removal effectiveness, air emissions from the process, cost, and process limitations.

The thin-film evaporator (TFE) study was a pilot-scale evaluation of the TFE for removal of VO from petroleum refinery wastes. The study was performed under different controlled conditions at three temperatures, three flow rates, and under both vacuum and atmospheric pressure. The removal of volatile compounds was greater than 99 percent, and the removal of semivolatiles ranged from 10 to 75 percent depending upon the processing conditions. When the system was operated under vacuum, some carryover of the feed resulted in a condensate that was a milky-white emulsion, which would require additional treatment to separate the oils and water. Vent rates from the condenser were found to depend on the type of waste and the quantity of light hydrocarbons, which are difficult to condense. The cost estimates for the TFE plus land treatment of the residuals yielded costs that were comparable to or less than the cost of land treating the original waste without pretreatment to remove VO.

Two full-scale steam strippers used to treat industrial wastewater containing about 6,000 ppm of purgeable VO were tested. The tray column stripper processed about 850 L/min of water that contained primarily ethylene dichloride and chloroform. Total VO removal averaged about 99.8 percent with an average concentration of 9.7 ppm in the bottoms. The condenser removed about 99 percent of the VO from the vapor and yielded a vent rate of about 20 Mg/yr. The packed column steam stripper processed about 42 L/min of water that contained primarily methylene chloride and chloroform. Total VO removal averaged 99.999 percent with an average concentration of less than 37 ppb in the bottoms. The condenser removed about 91 percent of the organic vapors and yielded a condenser vent rate of 11 Mg/yr. Emissions from the solids decanter and storage tank were estimated as 46 Mg/yr. The tray column stripper processed water containing 1.4 g/L of filterable solids compared to 0.01 g/L for the packed column. Costs for the small unit were confidential; the costs for the larger steam stripper were about $0.89/1,000 L treated.

The steam stripping/carbon adsorption unit was used to remove semivolatiles from water, which contained nitrobenzene, 2-nitrotoluene, and 4-nitrotoluene. Steam stripping reduced the concentration from 634 ppm to 48 ppm, a reduction of 92 percent. Liquid-phase carbon adsorption decreased the concentration in the bottoms to below detection limits (0.8 ppm) and yielded an overall removal efficiency of greater than 99.6 percent. Maximum air emissions were estimated as 35 kg/yr. The total cost of treatment was estimated as $8.90/1,000 L treated.

This report is submitted in partial fulfillment of EPA Contract Number 68-02-3992, Task 50, by Research Triangle Institute under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from April 1986 to May 1987, and work was completed as of June 1987.

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APPENDIX A

SAMPLING AND DATA COLLECTION PROCEDURES

APPENDIX A

SAMPLING AND DATA COLLECTION PROCEDURES

PROCEDURES FOR THIN-FILM EVAPORATOR PILOT STUDY

The TFE process consisted of the feed tank, feed pump, feed preheater, TFE, and condenser. Instrumentation for the process included thermocouples (Type K) for temperature measurements, oil heater control, and adjustable gear-driven Moyno positive displacement pump for flow control. The TFE rotor speed was constant during testing (1,300 r/min), and the preheater temperature was varied by adjusting the steam pressure to the preheater heat exchanger. The temperatures were measured by a multipoint temperature logger, with process temperatures read directly from the chart when the process was operating at a steady state. The bottoms and distillate flows were measured by collecting the material in collection buckets (bottoms) or flasks (distillate) over a timed interval. The amount of material collected was weighed and the flow rates calculated. The feed rate to the TFE was determined by summing the bottoms and distillate flow rates.

The TFE operating pressure was measured using a U-tube manometer adjacent to the apparatus, and the rotor current was measured by an ammeter attached to the TFE rotor's drive motor.

Figure A-1 shows the sampling points and process measurements for the TFE process.

Samples were taken in accordance with the Site Specific Test and Quality Assurance Plan (Contract 68-02-3992, W.A. No. 1-6, August 1986) to characterize the wastes treated during the pilot studies and to determine the efficiency and cost-effectiveness of the TFE process. Four process streams were sampled: feed (S1), bottoms (S2), condensate (S3), and condenser vent gas (S4). Table A-1 summarizes the number of samples taken during the testing, and Table A-2 lists the samples collected from these locations and the type of sample collected.

The feed (S1) was sampled from a sample port just after the Moyno feed pump. The valve for the sample port was opened, the sample line purged with a small amount of feed sludge, and the feed sludge samples were collected directly into clean amber bottles with Teflon-lined caps. Samples were sealed immediately after collection and refrigerated.

The process bottoms (S2) were collected in a bucket contained in a sealed pot directly under the TFE. The pot was sealed with the base of the TFE, preventing volatile loss and allowing the system to be under vacuum for the low-pressure runs. Bottoms were collected over a timed interval, and the collected bottoms were poured directly into clean amber sample jars after the

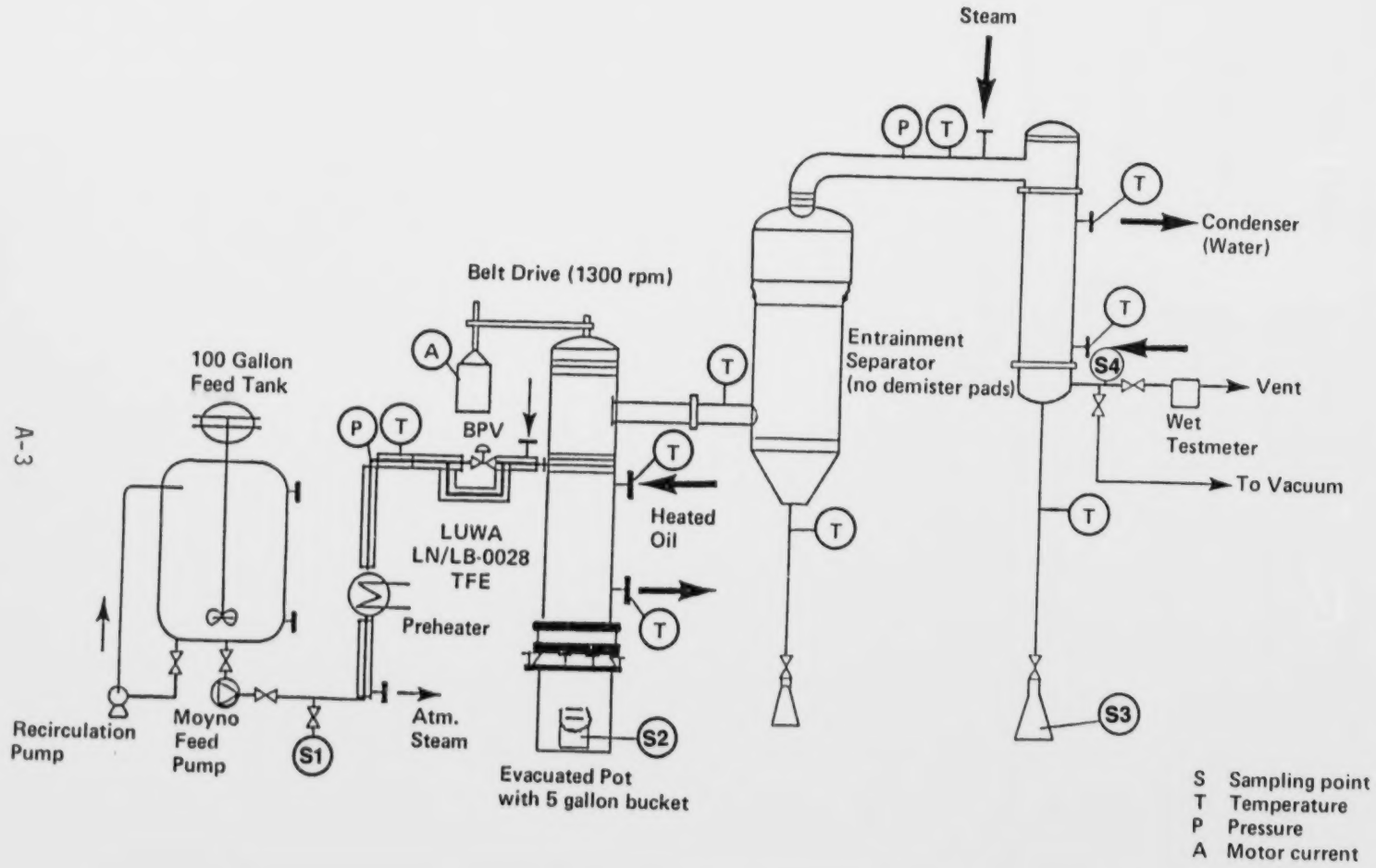

Figure A-1. Sampling and measurement points.

TABLE A-1. THIN-FILM EVAPORATOR SAMPLING

Location	Type	Number taken
S1-Feed sludge	1-L amber bottle	5
	500-cm^3 bottles (full)	9
	500-cm^3 bottles (1/2 full)[a]	5
S2-Bottoms	1-L amber bottle	24
	500-cm^3 bottles (full)	10
	500-cm^3 bottles (1/2 full)[a]	30
S3-Condensate	1-L amber bottles	26
S4-Vent gas	Evacuated S.S. canisters	7

[a]Used for onsite headspace analysis.

TABLE A-2. COLLECTED LIQUID AND GAS SAMPLES, LUWA THIN-FILM EVAPORATOR TESTS

Test number	Date - Time	Sample number	Description	Comments
	9/9/86 - 9:30 am	LUWA-24	S1, Feed 1 L full	Used material left
Feed	9/9/86 - 9:30 am	LUWA-25	S1, Feed 500 1/2	from first day of
Batch A	9/9/86 - 9:30 am	LUWA-26	S1, Feed 500 1/2	preliminary tests,
	9/9/86 - 9:30 am	LUWA-28	S1, Feed 500 full	drums #1 and #2.
1	9/9/86 - 9:30 am	LUWA-29	S3, Cond 1 L full	
1	9/9/86 - 9:30 am	LUWA-30	S2, Bott 1 L full	
1	9/9/86 - 9:30 am	LUWA-31	S2, Bott 500 1/2	
1	9/9/86 - 9:30 am	LUWA-32	S2, Bott 500 1/2	
2	9/9/86 - 10:05 am	LUWA-33	S3, Cond 1 L full	
2	9/9/86 - 10:05 am	LUWA-34	S2, Bott 500 1/2	
2	9/9/86 - 10:05 am	LUWA-27	S2, Bott 1 L full	
3	9/9/86 - 10:40 am	LUWA-35	S3, Cond 1 L full	
3	9/9/86 - 10:40 am	LUWA-36	S2, Bott 500 1/2	
3	9/9/86 - 10:40 am	LUWA-37	S2, Bott 500 1/2	
3	9/9/86 - 10:40 am	LUWA-38	S2, Bott 1 L full	
4	9/9/86 - 11:20 am	LUWA-39	S3, Cond 1 L full	
4	9/9/86 - 11:20 am	LUWA-40	S2, Bott 500 1/2	
4	9/9/86 - 11:20 am	LUWA-41	S2, Bott 1 L full	
	9/9/86 - 1:10 pm	LUWA-42	S1, Feed 1 L full	Drum #3 added to
Feed	9/9/86 - 1:10 pm	LUWA-43	S1, Feed 500 1/2	empty feed tank
Batch B	9/9/86 - 1:10 pm	LUWA-44	S1, Feed 500 1/2	
	9/9/86 - 1:10 pm	LUWA-45	S1, Feed 500 full	
5	9/9/86 - 1:10 pm	LUWA-46	S3, Cond 1 L full	
5	9/9/86 - 1:10 pm	LUWA-47	S2, Bott 500 1/2	
5	9/9/86 - 1:10 pm	LUWA-48	S2, Bott 1 L full	
5	9/9/86 - 2:40 pm	LUWA-63	S2, Bott 1 L full	
5	9/9/86 - 2:40 pm	LUWA-64	S3, Cond 1 L full	
5	9/9/86 - 2:40 pm	LUWA-65	S2, Bott 500 1/2	
5	9/9/86 - 2:40 pm	LUWA-66	S2, Bott 500 1/2	
5	9/9/86 - 2:40 pm	LUWA-67	S2, Bott 500 full	
5	9/9/86 - 2:40 pm	LUWA-68	S2, Bott 500 full	
5	9/9/86 - 2:50 pm	LUWA-69	S2, Bott 500 full	
5	9/9/86 - 2:50 pm	LUWA-70	S4, Vent Gas SS# A-60	
6	9/9/86 - 1:40 pm	LUWA-49	S3, Cond 1 L full	
6	9/9/86 - 1:40 pm	LUWA-50	S2, Bott 500 1/2	
6	9/9/86 - 1:40 pm	LUWA-51	S2, Bott 1 L full	

(continued)

TABLE A-2 (continued)

Test number	Date - Time	Sample number	Description	Comments
7	9/9/86 - 2:05 pm	LUWA-52	S3, Cond 1 L full	
7	9/9/86 - 2:05 pm	LUWA-53	S3, Cond 1 L full	
7	9/9/86 - 2:05 pm	LUWA-54	S2, Bott 1 L full	
7	9/9/86 - 2:05 pm	LUWA-55	S2, Bott 1 L full	
7	9/9/86 - 2:05 pm	LUWA-56	S2, Bott 500 1/2	
7	9/9/86 - 2:05 pm	LUWA-57	S2, Bott 500 1/2	
7	9/9/86 - 2:05 pm	LUWA-58	S2, Bott 500 full	
7	9/9/86 - 2:05 pm	LUWA-59	S2, Bott 500 full	
7	9/9/86 - 2:05 pm	LUWA-60	S2, Bott 500 full	
7	9/9/86 - 2:23 pm	LUWA-61	S4, Vent gas, SS# A-160	
7	9/9/86 - 2:23 pm	LUWA-62	S4, Vent gas, SS# A-67	
Feed Batch C	9/10/86 - 8:30 am	LUWA-80	S1, Feed 8:30 am 1 L full	Drum #4 added to feed tank
	9/10/86 - 8:30 am	LUWA-81	S1, Feed 8:30 am 500 1/2	
	9/10/86 - 8:30 am	LUWA-82	S1, Feed 8:30 am 500 1/2	
	9/10/86 - 8:30 am	LUWA-83	S1, Feed 8:30 am 500 full	
8	9/10/86 - 9:10 am	LUWA-71	S3, Cond 1 L full	
8	9/10/86 - 9:10 am	LUWA-72	S3, Cond 1 L full	
8	9/10/86 - 9:10 am	LUWA-74	S2, Bott 1 L full	
8	9/10/86 - 9:10 am	LUWA-75	S2, Bott 500 1/2	
8	9/10/86 - 9:10 am	LUWA-76	S2, Bott 500 1/2	
8	9/10/86 - 9:10 am	LUWA-77	S2, Bott 500 full	
8	9/10/86 - 9:10 am	LUWA-78	S2, Bott 500 full	
8	9/10/86 - 9:10 am	LUWA-79	S2, Bott 500 full	
8	9/10/86 - 9:16 am	LUWA-84	S4, Vent gas SS# A-100	
8	9/10/86 - 9:18 am	LUWA-85	S4, Vent gas SS# A-104	
9	9/10/86 - 11:25 am	LUWA-86	S3, Cond 1 L full	
9	9/10/86 - 11:25 am	LUWA-87	S2, Bott 500 1/2	
9	9/10/86 - 11:25 am	LUWA-88	S2, Bott full	
10	9/10/86 - 11:55 am	LUWA-89	S3, Cond 1 L full	
10	9/10/86 - 11:55 am	LUWA-90	S3, Cond 1 L full	

(continued)

TABLE A-2 (continued)

Test number	Date - Time	Sample number	Description	Comments
10	9/10/86 - 11:55 am	LUWA-91	S2, Bott 1 L full	
10	9/10/86 - 11:55 am	LUWA-92	S2, Bott 1 L full	
10	9/10/86 - 11:55 am	LUWA-93	S2, Bott 500 1/2	
10	9/10/86 - 11:55 am	LUWA-94	S2, Bott 500 1/2	
10	9/10/86 - 11:55 am	LUWA-95	S2, Bott 500 full	
10	9/10/86 - 11:55 am	LUWA-96	S2, Bott 500 full	
10	9/10/86 - 11:55 am	LUWA-97	S2, Bott 500 full	
10	9/10/86 - 12:01 pm	LUWA-98	S4, Vent gas SS# A-115	
10	9/10/86 - 12:04 pm	LUWA-99	S4, Vent gas SS# A-178	
10	9/10/86 - 12:04 pm	LUWA-100	Blank canister SS# A-188	
11	9/10/86 - 2:35 pm	LUWA-101	S3, Cond 1 L full	Only limited amounts of bottoms produced on this vacuum run
11	9/10/86 - 2:35 pm	LUWA-103	S2, Bott 500 1/2	
	9/10/86 - 3:30 pm	LUWA-105	S1, Feed 1 L full	Drum #5 added to feed tank
Feed	9/10/86 - 3:30 pm	LUWA-106	S1, Feed 500 1/2	
Batch D	9/10/86 - 3:30 pm	LUWA-107	S1, Feed 500 1/2	
	9/10/86 - 3:30 pm	LUWA-108	S1, Feed 500 full	
12	9/10/86 - 4:00 pm	LUWA-109	Cond 1 L full	Preheater was off for runs #13 and 14
12	9/10/86 - 4:00 pm	LUWA-110	Bott 500 1/2	
12	9/10/86 - 4:00 pm	LUWA-111	Bott 1 L full	
13	9/10/86 - 4:40 pm	LUWA-112	Cond 1 L full	
13	9/10/86 - 4:40 pm	LUWA-113	Bott 500 1/2	
13	9/10/86 - 4:40 pm	LUWA-114	Bott 1 L full	
14	9/10/86 - 5:30 pm	LUWA-115	Cond 1 L full	LUWA-117 not collected
14	9/10/86 - 5:30 pm	LUWA-116	Bott 500 1/2	
15	9/10/86 - 5:50 pm	LUWA-118	Cond 1 L full	
15	9/10/86 - 5:50 pm	LUWA-119	Bott 500 1/2	
15	9/10/86 - 5:50 pm	LUWA-120	Bott 1 L full	
16	9/10/86 - 6:20 pm	LUWA-121	Cond 1 L full	
16	9/10/86 - 6:20 pm	LUWA-122	Bott 500 1/2	
16	9/10/86 - 6:20 pm	LUWA-123	Bott 1 L full	

(continued)

TABLE A-2 (continued)

Test number	Date - Time	Sample number	Description	Comments
17	9/10/86 - 7:30 pm	LUWA-124	Cond 1 L full	
17	9/10/86 - 7:30 pm	LUWA-125	Bott 500 1/2	
17	9/10/86 - 7:30 pm	LUWA-126	Bott 1 L full	
18	9/10/86 - 8:20 pm	LUWA-127	Cond 1 L full	
18	9/10/86 - 8:20 pm	LUWA-128	Bott 500 1/2	
18	9/10/86 - 8:20 pm	LUWA-129	Bott 1 L full	
Feed Batch E	9/11/86 - 9:15 am	LUWA-130	S1, 1 L full Waste #2	Two barrels of the second waste were added to the empty feed tank
	9/11/86 - 9:15 am	LUWA-131	S1, 500 1/2	
	9/11/86 - 9:15 am	LUWA-132	S1, 500 full	
19	9/11/86 - 9:35 am	LUWA-133	S3, Cond 1 L full	
19	9/11/86 - 9:35 am	LUWA-134	S2, Bott 500 1/2	
19	9/11/86 - 9:35 am	LUWA-135	S2, Bott 1 L full	
20	9/11/86 - 10:30 am	LUWA-136	S3, Cond 1 L full	
20	9/11/86 - 10:30 am	LUWA-137	S2, Bott 500 1/2	
20	9/11/86 - 10:30 am	LUWA-138	S2, Bott 500 full	
21	9/11/86 - 12:15 pm	LUWA-139	S3, Cond 1 L full	
21	9/11/86 - 12:15 pm	LUWA-140	S2, Bott 500 1/2	
21	9/11/86 - 12:15 pm	LUWA-141	S2, Bott full 1 L	
22	9/11/86 - 1:00 pm	LUWA-142	S3, Cond 1 L full	
22	9/11/86 - 1:00 pm	LUWA-143	S2, Bott 500 1/2	
22	9/11/86 - 1:00 pm	LUWA-144	S2, Bott full 1 L	

bottoms were weighed. The bottoms were relatively hot as collected, and some very minor amount of VO compounds was lost during this transfer. The concentration of VO in the pot was measured frequently during the testing with a Bacharach hydrocarbon analyzer and was typically near 200 ppm. The low concentration of hydrocarbons directly above the bottoms samples after exposure to the air, the relatively high viscosity of the samples, and rapid transfer of collected samples to the sample containers ensured that the loss of volatiles was insignificant during collection. Samples were rapidly covered with Teflon-lined caps and refrigerated.

Collection of condensate samples during testing required special precautions to ensure that representative condensate samples were collected. Vapors condensing to liquids formed both an organic layer and an aqueous layer. Any holdup of liquid between the condenser and collection flasks split condensate into two fractions, with sample flowing from the system being nonrepresentative of the actual condensate. Condensing liquid flowed directly into sample collection bottles with no holdup of condensate, allowing samples to be collected as two layers that were representative of the condensate. Samples were collected by placing clean 1-L amber bottles directly under the sample port as the condensate flowed out of the condenser. Sampling continued until the collection bottle was full, then it was sealed with a Teflon-lined cap and refrigerated. These condensate samples were later split into the organic and aqueous fractions. Samples that were prepared from collected samples prior to analysis are listed in Table A-3. Volumes and weights of aqueous and organic fractions were measured during the sample splitting. The density of each fraction and the relative amounts of each fraction were determined from these data.

Gas canister samples were taken directly from the condenser vent directly after the condenser. The gas canisters were evacuated stainless steel canisters that were cleaned and evacuated as described in the QA plan. The vacuum was first checked on the canisters prior to sample collection, then a sampling port valve to the condenser vent was opened to permit vent gas to flow into the gas canister. The valve on the sample canister was then closed and the canister sealed with a Swagelok plug prior to shipment of the samples to the analytical laboratory.

PROCEDURES FOR PLANT I

Details on sampling procedures can be found in Section 3 of the site-specific test and QA plan dated September 12, 1986. A summary is provided in this section. The test was conducted September 23-25, 1986.

The field test included the collection of process data throughout the test and the collection of liquid and vapor samples for analysis. Process data included the feed flow rate and temperature, steam flow rate and temperature, cooling water temperature, column pressure drop, heat exchanger temperatures, and outage measurements for the holding tanks.

Samples of the stripper feed, bottoms, and condensate were taken five times at approximately 2-hour intervals during the day shift for each day of the 2-day test for VO analysis. These sample points are identified as S5, S6,

TABLE A-3. SAMPLES SPLIT FROM COLLECTED SAMPLES
(Runs 5, 7, 8, 10)

Sample number	Test number	Description	Split from sample
LUWA-145	5	Cond Aq 500 mL	LUWA-64 and 46
LUWA-146	5	Cond Aq 500 mL	LUWA-64 and 46
LUWA-147	5	Cond Aq VOA 40 mL	LUWA-64 and 46
LUWA-148	5	Cond Aq VOA 40 mL	LUWA-64 and 46
LUWA-149	5	Cond Org VOA 40 mL	LUWA-64 and 46
LUWA-150	5	Cond Org VOA 40 mL	LUWA-64 and 46
LUWA-151	5	Cond Org 500 mL	LUWA-64 and 46
LUWA-152	7	Cond Aq 500 mL	LUWA-52 and 53
LUWA-153	7	Cond Aq 500 mL	LUWA-52 and 53
LUWA-154	7	Cond Aq VOA	LUWA-52 and 53
LUWA-155	7	Cond Aq VOA	LUWA-52 and 53
LUWA-156	7	Cond Org VOA	LUWA-52 and 53
LUWA-157	7	Cond Org VOA	LUWA-52 and 53
LUWA-159	7	Cond Org 500 mL	LUWA-52 and 53
LUWA-160	8	Cond Aq 500 mL	LUWA-71 and 72
LUWA-161	8	Cond Aq 500 mL	LUWA-71 and 72
LUWA-162	8	Cond Aq VOA	LUWA-71 and 72
LUWA-163	8	Cond Aq VOA	LUWA-71 and 72
LUWA-164	8	Cond Org VOA	LUWA-71 and 72
LUWA-165	8	Cond Org VOA	LUWA-71 and 72
LUWA-166	8	Cond Org VOA	LUWA-71 and 72
LUWA-169	10	Cond Aq 500 mL	LUWA-89 and 90
LUWA-168	10	Cond Aq 500 mL	LUWA-89 and 90
LUWA-170	10	Cond Aq VOA	LUWA-89 and 90
LUWA-171	10	Cond Aq VOA	LUWA-89 and 90
LUWA-172	10	Cond Org VOA	LUWA-89 and 90
LUWA-173	10	Cond Org VOA	LUWA-89 and 90
LUWA-174	10	Cond Org 500 mL	LUWA-89 and 90
LUWA-175	5	Bott VOA	LUWA-67
LUWA-176	5	Bott VOA	LUWA-67
LUWA-177	7	Bott VOA	LUWA-58
LUWA-178	7	Bott VOA	LUWA-58
LUWA-179	8	Bott VOA	LUWA-77
LUWA-180	8	Bott VOA	LUWA-77
LUWA-181	10	Bott VOA	LUWA-95
LUWA-182	10	Bott VOA	LUWA-95

(continued)

TABLE A-3 (continued)

Sample number	Test number	Description	Split from sample
LUWA-183		Feed 4th Drum VOA	LUWA-80
LUWA-184		Feed 4th Drum VOA	LUWA-80
LUWA-185		Feed 4th Drum 500 mL	LUWA-80
LUWA-186		Feed 3rd Drum VOA	LUWA-42
LUWA-187		Feed 3rd Drum VOA	LUWA-42
LUWA-188		Feed 3rd Drum 500 mL	LUWA-42

and S7 in Figure 4-1. In addition, samples for headspace analysis were taken at each point. Composite samples were taken from S5 and S6 for filterable solids and dissolved solids. Composite samples from S5 also were analyzed for metals. Preliminary samples from S5 were taken to determine if any extractable organics were present in the wastewater. The pH and temperature of the liquid samples were measured several times during each test day.

Samples for VO also were taken around the initial solids decanters. The wastewater feed to the decanter (S1) was sampled throughout the first test day when wastewater was being pumped into the decanter. This wastewater also was analyzed for filterable and dissolved solids, metals, and VO in the headspace. Samples of the organic layer (S2) were taken for VO analysis, VO in the headspace, and filterable and dissolved solids. Samples of the sludge (S3) were taken for VO analysis, VO in the headspace, total solids, and for analysis by EPA's toxicity characteristic leaching procedures (TCLP). The wastewater decanted from the tank was sampled for VO, VO in the headspace, filterable solids, and dissolved solids.

The liquid samples for VO were taken in 40-milliliter (mL) glass VOA vials with septa and no headspace. Samples for extractable organics were taken in 1-liter (L) amber glass bottles with no headspace. The samples for solids and metals were taken in 0.5-L plastic bottles, and the metals samples were acidified to a pH < 2 with redistilled HNO_3. All samples were shipped packed in ice.

Vapor samples were taken three times each test day from the primary condenser vent (S8), secondary or tank condenser vent (S9), and the vent of the stripper's feed (storage) tank (S10). Vapor samples also were collected over the open organic collection tank (S11) and from the decanter vent prior to the vent condenser (S12). The vapor samples from the condensers were taken in evacuated electropolished stainless steel canisters. Before each vapor sample was taken, the presence of a vacuum was confirmed by connecting a vacuum gauge and recording the vacuum reading. When the vapor flowrates were sampled, the overflow pipes on the decanter were taped closed and the conservation vents were monitored to be certain that they remained closed.

PROCEDURES FOR PLANT H

Details on sampling procedures can be found in Section 3 of the site-specific test and quality assurance plan dated July 7, 1986. A summary is provided in this section. The test was conducted July 21-23, 1986.

General Samples

The field test included the collection of process data throughout the test period and the collection of samples for analysis. Process data were recorded by plant personnel and included the flow rate and temperature of the feed stream to the stripper, the flow rate and temperature of the bottoms stream from the stripper, the flow rate and pressure of the steam, and the supply temperatures of the cooling water and refrigerated glycol. In addition, the

plant installed an orifice flow meter to measure the rate of condensate collection. These data were recorded at one-half hour intervals throughout each test day.

Samples of the stripper feed, bottoms, and condensate were taken 5 times at 2-hour intervals (time = 0, 2, 4, 6, and 8 hours) during the day shift for each day of the 2-day test for VO analysis. These sample points are identified as S1, S2, and S3 in Figure 4-2. The condensate separated into an aqueous phase and a heavier organic phase (primarily EDC). The volumes of each phase were recorded, and samples of both the aqueous layer and the organic layer were submitted for analysis. Samples for extractable organics, solids, and metals were taken each hour during the test. The extractable organic samples were composited over a 4-hour period to yield 2 samples per day at each point, and the samples for solids and metals were composited over an 8-hour period to yield one sample per day. The pH and temperature of the liquid samples were also measured several times during each test day.

Samples of vapor from each of the two condensers were taken at S4 and S5 in Figure 4-2. Three samples from each point were taken each day at time = 0, 4.5, and 8 hours in evacuated stainless steel canisters.

The samples for VO were taken in 40-mL glass VOA vials with septa and no headspace. Samples for extractable organics were taken in 1-L amber glass bottles with no headspace. The samples for solids and metals were taken in 0.5-L plastic bottles, and the metals samples were acidified to a pH < 2 with redistilled HNO_3. All samples were shipped packed in ice and were analyzed within 14 days of the sample collection time.

The vapor samples from the condensers were taken in evacuated electropolished stainless steel canisters. Before each vapor sample was taken, the presence of a vacuum was confirmed by connecting a vacuum gage and recording the vacuum reading. The vapor sample line was purged briefly before sample collection.

Tracer Gas Samples

A tracer gas dilution technique was used to measure the vapor flow rate after the refrigerated glycol condenser because this was a closed system under pressure that was vented to an incinerator. Pure propane gas was metered into sample point S5 with a tracer injection system consisting of a propane gas cylinder, pressure regulator, check valve, flow controller, and Teflon transfer line. The flow controller was calibrated in the laboratory at RTI by measuring the flow of propane at specific flow controller set points with a soap film flowmeter. The flow controller is capable of delivering constant flow with a constant upstream pressure and varying downstream pressure as long as a minimum of 10 psig pressure differential is maintained. The upstream pressure was held at 40 psig with the pressure regulator and downstream pressure (i.e. duct pressure) was approximately 4 psig.

Samples of overhead vapor were collected from sample point S4 and analyzed for propane by gas chromatography with flame ionization detection. Two techniques were used for sampling on the first test day. The first involved

purging a 500 cc glass flask with vapor by connecting one end of the flask to the sample port, opening both stopcocks (one at each end), opening the sample port shut-off valve, and observing the flask outlet until vapor flow was evident. The flask was then sealed and transported to the mobile lab for analysis. The second sampling technique involved purging the sample port transfer line until vapor flow was observed, attachment of a silicone rubber septum to a 1/4 inch union on the port with a Swagelok nut and back ferrule, and withdrawal of vapor samples via a one cubic centimeter gas sampling syringe. The syringe was equipped with a shut-off valve to allow transport of sample to the lab for analysis without loss of syringe contents. All samples collected on the second test day were collected in the gas-tight syringe with a minimum flow rate used to purge the sample port prior to sample collection.

PROCEDURES FOR PLANT G

The objective of this sampling program is to determine how effectively the whitewater at Plant G is treated. Determinations are made using steam stripping of the water, followed by carbon adsorption. Samples of the feed water, organic condensate, aqueous condensate, steam stripper liquid effluent, and carbon adsorber effluent were collected during the steady-state operation of the steam stripper-carbon adsorber. Gas samples of the condenser vent were also collected.

Liquid Samples

Liquid samples from the steam stripper were collected from the sample lines into 40-mL volatile organic analyzer (VOA) bottles. The samples of the column feed and discharge and the carbon adsorption unit discharge were taken from appropriate process lines by filling a sample collection bottle. The liquid was then transferred to a VOA bottle. An additional sample was collected from the waste feed stream in a 1-L glass bottle for determination of pH and solids content.

Liquid samples were collected from the condensate collection vessel by draining the material received from the separator into a 1-L collection bottle equipped with a funnel. A 40-mL VOA bottle was then filled for volatiles determination.

Vent Gas Samples

Air samples from the condenser vent were collected in evacuated steel canisters. The evacuated sampling containers were connected to a vacuum gauge in the field, and the presence of a vacuum was confirmed. The pressure reading on the vacuum gauge was recorded. The sampling container was connected to a flexible tube that terminated in the vent. The valve was opened on the sampling container, and the container was filled with gas from the sampling location. The sample valve was then closed, the 1/4-inch Swagelok fitting was capped with a brass plug, and the sample description written on the sample container label.

APPENDIX B

SUMMARY OF ADDITIONAL MEASUREMENTS

APPENDIX B

SUMMARY OF ADDITIONAL MEASUREMENTS

ADDITIONAL MEASUREMENTS AT PLANT I

The additional measurements made at Plant I included evaluation of the removal of solids and metals in the decanter, mass and energy balances for the process, and estimate of Henry's law constants for the untreated wastewater.

The vapor-liquid equilibrium constant was estimated from the vapor canister analyses for the storage tank (S10) and the average liquid-phase concentration measured in the feed from the storage tank. The wastewater had been in the storage tank for several days; consequently, the vapor samples taken from the tank's headspace should represent equilibrium with the tank's liquid contents. The vapor samples from S10 contained percent levels of the chlorinated compounds with average vapor-phase concentrations of 382 mg/L for methylene chloride, 140 mg/L for chloroform, 48 mg/L for carbon tetrachloride, and 3.9 mg/L for chloromethane. The equilibrium constant calculated from the measured vapor and liquid concentrations in the storage tank are given in Table B-1. The comparison of the measured values with theoretical values of Henry's law constant shows reasonable agreement, although the measured values are less than the predicted values for all compounds.

The feed to the solids decanter (S1) was sampled for VO during the first test day when water was pumped from collection sumps into the decanter. On the second test day, no samples were taken because no water was pumped into the decanters. The results are given in Table B-2 and show that the major components are methylene chloride and chloroform. The average methylene chloride concentration at S1 was 2,970 ppm, the average concentration of chloroform was 1,770 ppm, and the average total VO in the wastewater at S1 was 4,820 ppm.

The results of samples taken from the water in the solids decanter (S4) before and after the settling period are given in Table B-3. The settling appears to decrease the VO concentration slightly. The concentration of methylene chloride in the decanter (3,800 to 5,420 ppm) is comparable to the concentration measured in the storage tank (3,419 to 6,788 ppm). Similar results are found for chloroform with levels of 1,630 to 2,283 ppm in the solids decanter and 864 to 2,829 ppm in the storage tank.

The sludge samples (S3) were analyzed by two different laboratories with the results shown in Table B-4. The measured levels of methylene chloride ranged from 4 to 20 percent (by weight), and the levels of chloroform ranged from 4.6 to 9.8 percent. Carbon tetrachloride was the other major VO component of the sludge with levels of 4 to 11 percent. The sludge was a viscous

TABLE B-1. VAPOR-LIQUID EQUILIBRIUM DATA

Compound	Vapor-liquid equilibrium constant at 25 °C	
	Measured[a] ($atm \cdot m^3/g \cdot mol$)	Theoretical[b] ($atm \cdot m^3/g \cdot mol$)
Chloromethane	2.9×10^{-3}	8.1×10^{-3}
Methylene chloride	2.1×10^{-3}	3.2×10^{-3}
Chloroform	2.7×10^{-3}	3.4×10^{-3}
Carbon tetrachloride	2.1×10^{-2}	3.0×10^{-2}

[a]Measured from vapor space analysis of the storage tank and analyses of the feed stream from the storage tank.

[b]Value for Henry's law constant in aqueous solution from OAQPS data base.

TABLE B-2. RESULTS FOR VOLATILE ORGANICS IN FEED TO SOLIDS DECANTER (S1)[a]

Time	Methylene Chloride	Chloroform	Carbon tetrachloride	1,1,2-Trichloroethane	Total
9:30	3,990	2,630	94.5	6.3	6,720
9:30[b]	1,250	967	73.9	3.4	2,290
11:00	1,520	1,220	23.9	6.0	2,770
13:00	5,110	2,280	81.8	10.3	7,480
Average	2,970	1,770	68.5	6.5	4,820

[a]All results in parts per million.

[b]Sample taken immediately after collection of first sample.

TABLE B-3. VOLATILE ORGANICS IN WATER FROM SOLIDS DECANTER (ppm)[a]

Location	Chloromethane	Methylene chloride	Chloroform	Carbon tetrachloride	1,1,2-Trichloroethane	Total VO
North decanter (S4)						
Before treatment	39	4,670	1,640	144	8.0	6,500
After treatment	20	3,800	1,630	28	5.9	5,480
South decanter (S4)						
Before treatment	17	5,420	2,283	136	6.0	7,860
After treatment	12	4,780	2,150	114	5.2	7,060

[a]Samples were taken before and after treatment. Treatment included addition of flocculant, mixing, and settling for solids and organic phase separation.

TABLE B-4. RESULTS OF SLUDGE ANALYSIS FOR VOLATILE ORGANICS
(percent unless otherwise noted)

1. IEA Results

Compound	Sludge from Day 1	Sludge from Day 2
Methylene chloride	19.6	8.0
Chloroform	9.8	4.7
Carbon tetrachloride	a	7.2

2. E and E Results

Compound	Sludge from Day 1	Sludge from Day 2
Methylene chloride	17.0	4.4
Chloroform	9.2	4.6
Carbon tetrachloride	4.1	11
Chloromethane[b]	99.7	170
Trichloroethylene[b]	--	380
1,1,2-Trichloroethylene[b]	413	407

[a]Not detected and detection limit not determined. However, a spike of 3.2 percent carbon tetrachloride resulted in 60-percent recovery.

[b]These results are in parts per million.

material with pockets of an organic phase dispersed in the solids. Consequently, obtaining representative samples during sampling and analysis is difficult and may contribute to imprecision in the sludge analyses.

The organic layer from the solids decanter (S2) and from the steam stripper decanter (S7) also were analyzed for VO. The results listed in Tables B-5 and B-6 show that methylene chloride and chloroform are the major components. Other VO constituents that may have been present at much smaller levels could not be identified and quantified because of the loss of sensitivity to quantify the two major components and because of the large tailing peaks of methylene chloride and chloroform.

Several samples were analyzed for metals content, with the results given in Table B-7. The feed to the solids decanter (S1) was sampled throughout the first test day when rainwater was being collected in the sumps. This sample is untreated and yielded the highest concentration of metals. Samples also were taken from the solids decanter before and after a treatment step that includes flocculation and settling. The treatment appeared to decrease the levels of cadmium, chromium, copper, nickel, lead, and zinc in the wastewater that was transferred eventually to the storage tank for steam stripping.

The results for solids content given in Table B-8 are inconclusive. The results for the South decanter show a significant decrease in filterable solids (1,079 to 50 ppm). However, the results for a batch of wastewater in the North decanter appear to show an increase in filterable solids. The batch in the North decanter during the test was very troublesome because of difficulty in adjusting the pH and in obtaining a clear separation. The anomalous results for the North decanter may have arisen from these difficulties and the inability to collect samples that were known to be representative.

The solids results for the stripper feed and bottoms show that the levels of dissolved and filterable solids are much lower than the levels measured in the solids decanter, which may result from variations among different batches. The small decrease in solids concentration between the feed and bottoms suggests that there may be a small net accumulation of solids in the steam stripping process.

The sludge (S3) also was analyzed for solids. The results given in Table B-9 reveal levels of 11 to 24 percent solids. EPA's TCLP also was performed on the sludge. The results in Table B-10 show that very high levels of the three major compounds were found in the extract from the TCLP. These concentrations were essentially determined by the compound's solubility in the extracting fluid. This was confirmed in the laboratory when attempts to spike the extracting fluid with additional VO resulted in a phase separation. The TCLP results for metals are given in Table B-11. The major metals found from the TCLP were nickel (59 to 83 ppm), zinc (36 to 57 ppm), and iron (10 to 28 ppm).

The primary purpose of the initial decanters is to remove any separate organic phase and solids from the wastewater prior to steam stripping. During the test, the filterable solids in the stripper feed ranged from 10.7 to 12 mg/L. The processing of two batches of wastewater in the decanters

TABLE B-5. ANALYSIS OF DECANTED ORGANIC LAYER FROM S2 (g/L)

Test day	Time	Methylene chloride	Chloroform
1	9:30	1,200	495
1	14:30	920	362
2	12:10	890	449
	12:10	892	387
	12:10	917	405
Average		964	420

TABLE B-6. ANALYSIS OF ORGANIC CONDENSATE FROM S7 (g/L)

Run number	Methylene chloride	Chloroform
1-1	1,180	309
1-2	1,290	306
1-3	1,100	269
1-4	1,160	313
1-5	1,250	322
2-1	970	269
2-2	1,130	308
2-3	1,110	321
2-4	1,250	318
2-5	1,260	400
2-6	1,320	378
Average	1,180	319

TABLE B-7. RESULTS OF ANALYSES FOR METALS (ppb unless otherwise noted)

Metal	Stripper feed (S5) Day 1	Stripper feed (S5) Day 2	Solids decanter (S1) feed for Day 1	Solids decanter (S4) (mixed)	Solids decanter (S4) (after treatment)
Arsenic	<1.0	8.7	179	8.3	8.1
Beryllium	0.52	0.99	4.6	1.6	1.5
Cadmium	8.0	<0.1	151	29	<0.1
Chromium	2.5	5.0	19,400	1,800	53
Copper	73	53	3,611	572	122
Mercury	a	a	a	a	a
Nickel[b]	1.7	0.07	86.2	12.7	0.39
Lead	2.2	<1.0	429	72.6	6.0
Selenium	<2.0	<2.0	<2.0	<2.0	<2.0
Zinc[b]	0.26	0.35	53.8	6.6	1.1

[a]Not detected at a level of 4 ng.

[b]Results for nickel and zinc are in parts per million.

TABLE B-8. RESULTS FOR TOTAL AND FILTERABLE SOLIDS (ppm)

Location	Dissolved solids	Filterable solids
South decanter (S4)		
Before treatment[a]	11,600	1,079
After treatment	17,600	50
North decanter (S4)		
Before treatment	45,000	51
After treatment	40,400	208
Stripper feed (S5)		
Day 1	4,600	10.7
Day 2	6,200	12.0
Stripper bottoms (S6)		
Day 1	4,160	9.5
Day 2	5,930	8.0

[a]Treatment includes addition of flocculant, mixing, and settling in decanter.

TABLE B-9. RESULTS FOR ANALYSIS OF TOTAL SOLIDS IN SLUDGE (S3)

Test day	Percent solids
1	11.1
1	13.1
1	11.9
2	24.4

TABLE B-10. RESULTS OF TOXICITY CHARACTERISTIC LEACHING PROCEDURE ON SLUDGE FOR VOLATILE ORGANICS (ppm)[a]

Compound[b]	Sludge from Day 1[c]	Sludge from Day 2	Blank
Carbon tetrachloride	213	380	0.22
Methylene chloride	7,070	3,700	0.043
Chloroform	2,600	1,700	0.008

[a]Analysis of extract (simulated leachate) from decanter sludge.

[b]No other volatile compounds were detected at a limit of approximately 250 ppm.

[c]Average of 3 replicates.

TABLE B-11. RESULTS OF TOXICITY CHARACTERISTIC LEACHING PROCEDURE ON SLUDGE FOR METALS (ppm)[a]

Metal	Sludge from Day 1[b]	Sludge from Day 2
Arsenic	<0.04	<0.04
Barium	0.59	0.015
Beryllium	0.003	0.007
Cadmium	0.18	0.188
Chromium	0.107	0.248
Copper	0.345	0.103
Iron	10.4	28.1
Lead	<0.02	0.03
Mercury	0.0005	0.0012
Nickel	59.4	83.4
Selenium	<0.04	<0.04
Silver	<0.01	<0.01
Zinc	36.2	57

[a]Analysis of extract from decanter sludge.

[b]Average of 3 replicates.

revealed solids levels of 50 to 208 mg/L after treatment. Because of the many sources of wastewater, including runoff from rain, solids levels are likely to vary from batch to batch. The process appeared to be effective in reducing the solids content because fouling of the packed column was not a problem during the test and has not been a significant problem for the plant, according to company personnel. The solids removal step also decreased the levels of cadmium, chromium, copper, nickel, lead, and zinc in the wastewater. Consequently, solids removal prior to steam stripping resulted in lower concentrations of metals in the effluent as well as improved consistency in the steam stripper's performance and fewer problems from fouling of the packing material.

The decanter is also designed to remove any separate organic phase. This step should also improve the consistency of operation and performance of the steam stripper. A slug of a separate organic phase in the feed could cause flooding, high concentrations in the bottoms, and other operational problems. Data supplied by the company indicated that roughly 50 Mg/yr of a separate organic phase is removed from the initial decanters. The generation of sludge was estimated as 220 Mg/yr with a water treatment rate of 16,500 Mg/yr (based on 11 gal/min for 75 percent of the year).

A summary of the process data collected during the 2-day test is given in Table B-12. The feed rate to the stripper and the steam rate shows very little variation (<5 percent) throughout each test day. For the first test day, the feed rate averaged 41 L/min (10.8 gal/min) and the steam rate averaged 252 kilograms per hour (kg/h) or 555 pounds per hour (lb/h). On the second test day, the feed rate averaged 40.5 L/min (10.7 gal/min) with a steam rate of 254 kg/h (559 lb/h). The rate of steam usage was about 0.1 kg/kg water. The pH of the feed and bottoms was consistently at 5.0 during the first test day. No water was added to the feed (storage) tank during the first test. Prior to the second test, a batch of wastewater was transferred from the solids decanter with a very high pH after caustic addition. Throughout the second test, the pH of the feed and bottoms was 11.3 to 11.6.

The process data were used to estimate the distribution of mass and energy around the steam stripper. The results are summarized in Table B-13. The mass flowrates of the feed, steam, and vapor were measured directly. Attempts to measure the condensate rate directly were hampered by an inability to empty the decanter completely, inaccuracies because of separate phases and a partially suspended organic phase, and the continuous generation of condensate.

Because only a pure organic phase is removed from the system as condensate, the condensate rate was estimated from the amount of organics entering with the feed minus the amount of organics leaving with the vapors from the condenser vent. (Organics in the bottoms from the stripper were negligible.) An attempt was made to measure the bottoms rate by measuring the change in volume of the holding tanks as a function of time. This approach was not very accurate and resulted in highly variable rates. The bottoms rate presented in Table B-13 was estimated from the total in (feed and steam) minus the quantity leaving with the condensate and vapors.

TABLE B-12. SUMMARY OF PROCESS DATA

Parameter	9-24-86	9-25-86
Steam rate (kg/h)	252	254
Feed rate (kg/h)	2,450	2,430
Bottoms rate (kg/h)	2,690	2,670
Pressure drop (mm H_2O)	267	292
Feed pH	5.0	11.5-11.6
Bottoms pH	5.0	11.3-11.5
Cooling water temperature (°C)	17-20	18-21
Condensate temperature (°C)	18-22	18-22
Heat exchanger temperatures (°C)		
Feed in	24	26
Feed out	82	79
Bottoms in	98	99
Bottoms out	41	46
Bottoms temperature (°C)[a]	108	105

[a]Bottoms temperature recorded by plant.

TABLE B-13. DISTRIBUTION OF MASS AND ENERGY

Stream	9-24-86		9-25-95	
	kg/h	10^6 Btu/h	kg/h	10^6 Btu/h
Feed	2,450	0.799	2,430	0.760
Steam	252	0.641	254	0.650
Total in	2,700	1.44	2,680	1.41
Bottoms	2,690	1.15	2,670	1.11
Condensate[a]	12	b	12	b
Vapors	1.2	b	1.2	b
Cooling water[c]	--	0.290	--	0.300
Total out	2,700	1.44	2,680	1.41
Recycled condensate water[d]	114	--	118	--
Heat exchanger duty[e]	--	0.567	--	0.509

[a]Condensate rate estimated from organics in with feed minus organics out with uncondensed vapor and bottoms (negligible).

[b]Negligible contribution to overall balance.

[c]Heat removed by the condenser was estimated by difference (total in minus out with bottoms, vapor, and condensate).

[d]The rate of recycle for the condensed water was estimated from energy removed by the condenser divided by the latent heat of vaporization of water.

[e]Energy exchanged in heat exchanger based on feed flowrate and temperature increase.

The energy balance data show that the heat exchanger recovers and provides about 36 to 40 percent of the total energy entering the stripper. Heat is exchanged at a rate of 0.5 to 0.6 million Btu/h. The primary condenser removes about 0.3 million Btu/h from the overhead vapors.

All of the condensed water from this process is returned to the steam stripper. The rate of recycle was estimated from the energy balance as 114 to 118 kilograms per hour (kg/h) or about 5 percent of the feed rate.

ADDITIONAL MEASUREMENTS AT PLANT H

Additional measurements made by the sampling team are summarized in Table B-14 to correspond with the run numbers for the samples of wastewater entering and leaving the steam stripper. During the start of the test during the first day, the heat exchanger started to foul and the feed temperature was measured at 67 and 63 °C (for Runs 1-1 and 1-2). The heat exchanger and column were backflushed. After backflushing, the feed temperature increased to a range of 80 to 88 °C for the balance of the test. The data in Table B-14 also show an increase in pH in the wastewater after steam stripping.

The results for priority pollutant metals and solids are summarized in Table B-15. Copper was found at levels higher than any of the other metals and probably originates from the catalyst used in the production of 1,2-dichloroethane (see Section 3.0). The results for solids reveal levels in excess of 1 percent for dissolved solids and about 0.1 percent for suspended solids. The differences in concentrations between the feed and bottoms suggest that there may be a net accumulation of solids in the steam stripper and/or heat exchanger.

Overall mass and energy balances were performed on the steam stripper. During the morning of the first test day, some operating problems with the steam stripper were experienced because of fouling in the heat exchanger and column. The flow rates were quite variable during this period; consequently, this time period (7:30 to 10:30) was treated separately for the first test day. Flow rates were relatively consistent for the balance of the first test day (11:00 - 16:30) and throughout the second test day. Mass and energy balances were performed for these three time periods and are summarized in Table B-16.

The energy balances are based on the measured flow rates of each stream entering and leaving the stripper, the temperatures of the liquid streams, and steam at 50 psig (64.7 psia). Heat removal with the overhead vapors is based on saturated steam at 4 psig (the overhead pressure) being cooled to approximately 33 °C (the typical condensate temperature).

The mass balance results in Table B-16 for the time period 7:00 to 10:30 do not represent 100 percent closure because of wide ranging flow rates recorded at one-half hour intervals and the difficulty in obtaining a reasonably accurate average for the period. Flow rates were consistent for the balance of the test period and reasonably accurate averages could be obtained. The result is a percent closure approaching 100 percent and a high

TABLE B-14. TEMPERATURE, pH, AND CONDENSATE SEPARATION MEASUREMENTS

Run No.	Temperatures (°C)			pH			Volume Percent Organics in Condensates
	Influent	Effluent	Condensate	Influent	Effluent	Condensate	
1-1	67	42	32	6.7	8.7	6.3	18.3
1-2	63	39	31	7.3	9.0	6.2	18.8
1-3	85	40	33	5.2	9.2	6.2	17.0
1-4	84	38	35	7.0	9.0	6.3	15.0
1-5	84	40	35	8.7	8.9	6.0	14.0
2-1	81	43	33	6.0	8.8	6.0	11.4
2-2	80	43	34	7.0	9.3	6.2	20.6
2-3	81	41	35	7.1	5.6	6.2	12.1
2-4	87	48	39	5.0	6.5	6.2	10.0
2-5	84	41	36	4.9	8.6	6.4	12.1

TABLE B-15. RESULTS OF METALS AND SOLIDS ANALYSES
(All Results in ppms or mg/L)

Parameter	Test Day 1		Test Day 2	
	Feed	Bottoms	Feed	Bottoms
Arsenic	.031	.015	.044	.028
Cadmium	<.01	<.01	<.01	<.01
Chromium	.18	.14	.11	.12
Copper	33	34	31	38
Lead	<.005	<.005	<.005	<.005
Mercury	.007	.010	.007	.008
Nickel	.73	.54	.53	.52
Selenium	<.005	<.005	<.005	<.005
Zinc	1.2	.35	.30	.17
Antimony	<.2	<.2	<.2	<.2
Beryllium	<.01	<.01	<.01	<.01
Dissolved Solids[a]	13,000	11,000	14,000	12,000
Suspended Solids[a]	1,400	910	1,400	950

[a]These results represent only 2 significant figures.

TABLE B-16. MASS AND ENERGY BALANCES

Stream[a]	7/22/86 (7:00-10:30)[b]		7/22/86 (11:00-16:30)		7/23/86 (7:00-16:30)	
	Mass (Mg/h)	Energy (10^6 BTU/h)	Mass (Mg/h)	Energy (10^6 BTU/h)	Mass (Mg/h)	Energy (10^6 BTU/h)
Feed	45.7	12.5	51.0	15.9	49.5	16.1
Steam	3.9	10.2	1.6	4.2	1.8	4.6
Total In	49.6	22.7	52.6	20.1	51.3	20.7
Bottoms	41.4	17.9	51.9	22.0	50.7	20.7
Condensate	4.0	5.0	0.7	1.7	1.1	2.3
Total Out	45.4	22.9	52.6	23.7	51.8	23.0
Percent Closure[c]	109	99	100	85	99	90

[a]Mass and energy in the vented gas is negligible in comparison to major streams.

[b]This time interval was treated separately because of large fluctuations in flow because of column and heat exchanger fouling problems. Other time intervals represent steady operation.

[c]Defined as In ÷ Out x 100.

level of confidence in the distribution of mass for 7/22 (11:00 - 16:30) and 7/23.

The energy balances show reasonable percent closure values for an industrial process and the instrumentation involved. However, the differences in percent closure between the mass and energy balances for each period suggests a consistent bias in the energy balance, i.e., either the energy in is underestimated by about 10 percent or the energy out is overestimated by about 10 percent. The data were examined to assess probable causes of the bias in the energy balance. The column pressure was approximately 4 psig and corresponds to a vapor pressure of water of 18.7 psia. Water in equilibrium with its vapor at 18.7 psia has a temperature of 106.8 °C. This suggests that the measured temperature of the stripper bottoms (effluent) at 107-108 °C was accurate because it corresponds to the water temperature predicted at 4 psig or 18.7 psia (106.8 °C). Consequently, the feed temperature (entering the column after preheating in the heat exchanger) is suspected as the likely source of the bias. A sensitivity analysis was performed to assess the effects of small changes in mass flow rates and temperatures on the percent closure of the material and energy balances and the results are listed below. The first row ("overall") shows the percent closure based on the actual experimental results. The other rows show how the percent closure changes if the value of one of the parameters is altered.

Parameter Adjusted	Reported Value	Altered Value	Percent Closure	
			Mass	Energy
Overall	---	---	100	85
Feed temperature	80 °C	90 °C	100	94
Bottoms temperature	107 °C	100 °C	100	91
Steam rate	1.6 Mg/h	2.0 Mg/h	99.3	90
Condensate	0.6 Mg/h	0.3 Mg/h	99.4	89
Bottoms	51.9 Mg/h	50 Mg/h	96.4	89
Overhead temperature	102.5 °C	80 °C	100	86

The results given above suggest that an actual feed temperature slightly higher than the reported value yields a much better percent closure on the energy balance without affecting the percent closure on the mass balance.

The condensers for the overhead vapors remove energy from the system at a rate of roughly 1.7 to 2.3 million BTU's per hour. The condensers include a primary condenser that uses cooling tower water at approximately 29 °C followed by a refrigerated glycol condenser at approximately 2 °C. The second condenser probably represents the maximum cooling that can be supplied by condensers of this type because operation at temperatures below 2 °C could lead to freezing and fouling or plugging problems.

The heat duty of the plate and frame heat exchanger used to preheat the feed was estimated from the effluent flow rate and the temperature difference in the effluent entering and leaving the heat exchanger. The average flow

rate of effluent over the test period was approximately 51.3 Mg/h and the average temperature drop was from 108 °C to 43 °C. The heat exchanged under these conditions is approximately 13.2 million BTU's/h. The total energy entering the steam stripper from Table B-16 was about 20.4 million Btu's/h; consequently, the preheat heat exchanger recovers and supplies about 65 percent of the total energy needed for the operation. Because steam stripping is energy intensive and total operating costs are strongly affected by the cost of steam, the use of this heat exchanger represents significant energy and operating cost savings.

Mass balances were performed for two constituents that represent the two extremes in the pathway of removal from the process. Vinyl chloride is very volatile and condenser vent measurements showed that essentially all of the vinyl chloride left through the condenser vent and was routed to the incinerator. On the other extreme, essentially all (99+ percent) of the 1,2-dichloroethane entering with the wastewater is recovered with the condensate. Because the condensate rate was highly variable, averages from each test day were determined from Table B-17 and the quantity of 1,2-dichloroethane removed was estimated from a composition of about 90 percent in the organic phase and roughly 1.8 to 2.1 percent in the water phase. The most reliable and complete vent rate measurements were made on the second test day; therefore, the vinyl chloride rate through the condenser vent is probably most reliable for this time period. The mass balance results for vinyl chloride and 1,2-dichloroethane are given in Table B-18.

TABLE B-17. RATE OF CONDENSATE COLLECTION

Run No.	Total Condensate (gal/min)	% Organic by Volume[a]	Water Condensate Rate (g/s)	Organic Condensate Rate (g/s)[b]
1-1V	9.14	18.8	468	137
1-2V	4.0	16.6	211	52.8
1-3V	3.22	14.0	175	35.8
2-1V	4.69	11.4	262	42.5
2-2V	11.85	10.0	673	94.2
2-3V	4.10	12.1	227	39.4

[a]These values were averaged over time intervals that overlap or include the time at which the vapor samples were taken.

[b]Specific gravity = 1.26.

TABLE B-18. RATE OF VINYL CHLORIDE AND 1,2-DICHLOROETHANE
(All rates in g/s)

	Day 1	Day 2
	Average (95% limits)[a]	Average (95% limits)[a]
Vinyl chloride		
In with feed	.092[b] (.03 - .29)	.076 (.05 - .11)
Out condenser vent	.078[c] (.05 - .12)	.074 (.04 - .15)
1,2-Dichloroethane[d]		
In with feed	77 (45 - 130)	69 (49 - 97)
Out with organic condensate	68 (12 - 388)	58 (23 - 145)
Out with water condensate	5 (.7 - 34)	8 (2.2 - 29)
Out condenser vent	0.2 (.07 - .6)	0.4 (.2 - .8)
Total Out	73	66

[a]Confidence limits determined from propagation-of-error analysis. Assumes no bias in measurements of flow rates and concentrations and a log normal distribution for repeat measurements throughout the test day. The greatest uncertainty is in the mass rate of the compound in the condensate, which is estimated from three measurements (condensate flow rate, percent organics by volume, and concentration in the organic layer).

[b]Vinyl chloride concentrations in the feed were highly variable for the first test day and were fairly constant for the second test day. No vinyl chloride detected in the stripper bottoms.

[c]Based on only one measurement of the mass flow rate out of the condenser vent for the first test day. An average of 3 measurements were used for the second test day.

[d]The mass flow rate of 1,2-dichloroethane in the stripper bottoms was negligible (10^{-3} to 10^{-4} g/s).

APPENDIX C

PROCESS DATA

TABLE C-1. PROCESS DATA: STEAM STRIPPER, PLANT G[a]

Time	Steam (S)			Feed (F)
	Flow rate kg/h	Temperature °C	Pressure kPa	Flow rate kg/h
11:45	1,926	128.9	262	29,900
12:00	2,027	128.9	262	29,900
12:15	1,928	129.3	248	29,900
12:30	2,010	128.9	269	29,900
13:15	2,111	128.7	262	29,900
13:30	2,101	128.4	276	29,900
14:27	2,129	128.5	262	29,900
Average	2,033	128.8	263	29,900
Std. dev.	84	0.3	8.5	-

[a]These data were originally collected in units of lb/h, °F, psig, and gal/min.

TABLE C-2. PROCESS DATA: STEAM STRIPPER, PLANT G[a]

Time	Bottom level of liquid in column, %	Pressure at bottom of column, kPa	Heat exchanger temperature, °C		
			F1	F	B1
11:00	60	103	27	85	58
11:57	55	103	27	84	57
12:33	55	103	27	84	57
1:06	55	103	27	83	58
1:35	60	103	27	83	58
2:13	60	103	27	82	58
2:35	55	103	27	82	58
Average	57	103	27	83	58

[a]These data were originally collected in units of %, psig, and °F.

TABLE C-3. PROCESS DATA FOR PLANT H (FIRST TEST DAY)

Date: 7-22-86

Time	Stripper Feed		Stripper Bottoms		Steam to Stripper		Condensate	Cooling System Temperature (°C)	
								Cooling Tower Water	
	Flow (gal/min)	Temp. (°C)	Flow (gal/min)	Temp. (°C)	Flow (lbs/hour)	Pressure (psig)	Flow Rate (gal/min)	Supply	Return
0700	227.6	73	240	108	8,590	50	9.42	29	2
0730	225.6	55	240	108	8,710	50	9.40	29	2
0800	228.1	67	244	108	7,070	50	9.27	29	2
0830	233.6	61	170	111	9,910	50	9.40	29	2
0900	230.6	60	240	112	8,750	51	9.14	29	2
0930	119.0	78	80	119	10,600	50	40.47	29	2
1000	172.6	81	160	102	9,320	50	32.33	29	2
1030	172.5	77	80	106	6,020	50	23.21	29	2
1100	209	56	200	108	3,790	48	8.17	29	2
1130	241	65	216	107	4,460	51	4.15	29	2
1200	218	82	220	107	3,210	51	4.24	29	2
1230	217	91	220	108	3,190	50	4.60	29	2
1300	217	88	220	107	3,220	50	3.29	29	2
1330	232	84	232	108	4,690	50	2.76	28	2
1400	221	82	232	108	3,220	50	2.37	29	2
1430	224.7	81	220	107	3,270	50	3.35	29	2
1500	219	75	220	107	3,220	50	3.85	29	2
1530	225	76	240	107	3,220	50	1.67	29	2
1600	228	74	248	107	3,320	49	2.90	29	2
1630	225.8	73	240	108	3,670	49	3.22	29	2

TABLE C-4. PROCESS DATA FOR PLANT H (SECOND TEST DAY)

Date: 7-23-86

Time	Stripper Feed		Stripper Bottoms		Steam to Stripper		Condensate	Cooling System Temperature (°C)		
	Flow (gal/min)	Temp. (°C)	Flow (gal/min)	Temp. (°C)	Flow (lbs/hour)	Pressure (psig)	Flow Rate (gal/min)	Cooling Tower Water		Glycol
								Supply	Return	Supply Return
0700	231	a	240	107	4,600	50	4.34	29	36	2.2
0730	231		240	108	4,240	50	4.69	30	36	2.0
0800	228		232	108	4,210	50	4.69	30	36	2.0
0830	230		236	108	4,020	50	3.63	30	36	2.0
0900	229		232	109	4,550	50	4.10	29	36	2.2
0930	234		232	110	3,900	50	4.34	29	35	2.2
1000	227		226	111	4,300	50	3.74	29	35	2.0
1030	232		226	108	4,510	50	3.46	29	35	2.0
1100	225		232	108	3,690	50	3.85	29	35	2.0
1130	227		224	108	4,250	50	3.35	29	35	2.2
1200	227		232	108	4,150	50	4.52	28	33	2.0
1230	231		230	109	4,450	50	4.15	28	33	2.2
1300	209		230	112	3,990	50	12.54	28	34	2.0
1330	185		220	107	3,240	50	11.85	28	34	2.0
1400	197		200	108	3,210	50	4.43	28	34	2.2
1430	195		240	108	3,220	50	3.79	28	34	2.0
1500	191		180	107	3,260	50	4.52	28	35	2.0
1530	187		160	108	3,210	50	4.10	29	35	2.2

[a]Plant instrument malfunctioned. Feed temperature was measured by the sampling team with a thermometer and it ranged from 81-88 °C throughout the test.

TABLE C-5. PROCESS DATA FOR PLANT I (9/24/86)

Time	Steam Flow (lb/h)	Steam Flow Totalizer	Feed (gal/min)	Pressure drop (in. H_2O)	Bottoms temp. (C)	Holding tanks (inches) East	Holding tanks (inches) West	Decanter tanks (% full) North	Decanter tanks (% full) South	Storage tank (% full)
7:45	555	50598	10.8	10.5	104	139	32	76.5	32	30
8:30	555	50981	11.0	10.5	104	128	49	78	33	30
9:15	555	51431	10.8	10.5	104	20	70	85	35	30
9:45	555	51738	10.8	10.5	104	0	83	85.5	42	30
10:15	555	51961	10.8	10.5	104	0	94	86	44.5	30
11:00	555	52383	10.9	10.5	104	0	113	86	47	30
11:45	555	52734	10.8	10.5	104	0	128	88	47	30
12:30	555	53169	10.8	10.5	104	0	140	89	66	29
13:15	555	53359	10.9	10.5	104	0	139	94	83	29
14:00	560	53942	10.9	10.5	104	30	139	96	87.5	28.5
16:00	560	55111	10.8	10.5	104	87	100	96	82.5	28.5

TABLE C-6. PROCESS DATA FOR PLANT I (9/25/86)

Time	Steam Flow (lb/h)	Steam Flow Totalizer	Feed (gal/min)	Pressure drop (in. H_2O)	Bottoms temp. (C)	Holding tanks (inches) East	Holding tanks (inches) West	Decanter tanks (% full) North	Decanter tanks (% full) South	Storage tank (% full)
7:45	555	3550	10.9	11.5	105	0	68	94	88	25
8:45	565	4113	10.7	11.5	105	0	92	94	88	25
9:30	560	4482	10.6	11.5	105	0	108	94	88	25
10:30	560	4985	10.7	11.5	105	0	116	94	88	25
11:45	555	5717	10.2	11.0	105	22	138	94	88	24

APPENDIX D

ANALYTICAL PROCEDURES

APPENDIX D

ANALYTICAL PROCEDURES

ANALYTICAL PROCEDURES FOR THIN-FILM EVAPORATOR TEST

The analytical procedures for both the field analyses and the contracted analyses are discussed in this section. Analyses were performed by RTI personnel at the test facility and by two contract analytical laboratories, IEA and CompuChem.

The onsite measurements performed by RTI were: (1) the analysis of headspace concentrations of VO from feed sludge samples and bottoms samples and (2) the measurement of vent gas flow rates and overall VO concentrations in the vent gas and bottoms collection pot. Two types of analyses for headspace concentrations of VO were employed. The first used syringes to transfer gas samples from half-filled 500-cm^3 sample bottles and a portable GC to measure the concentrations of VO in air above the samples.

The samples for headspace analysis of VO compounds were half-filled 500-mL amber bottles with modified caps to allow gas sample removal through a septum on the bottle's cap. Samples were withdrawn from the bottle and injected into a GC with a flame ionization detector. The GC system is listed in Table 6-1. It was calibrated with both a C1 to C7 gas hydrocarbon standard (methane, ethane, propane, butane, pentane, and hexane 100 ppm in N_2) and a liquid benzene standard (200 μg/mL). Samples of toluene were injected to determine the retention time of the compound. The field analysis was conducted without knowing the specific organic compounds that would be present in the samples. The compound peaks were identified by the retention times of eluting compounds, and the identification was confirmed by GC/MS analysis of headspace samples by IEA. The headspace samples were found to contain propane, butane, pentane, hexane, benzene, and toluene. Also detected were 2-butene, cyclopentane, 2-methyl pentane, and 2-methyl butane in substantial concentrations. The operating manual for the GC can be found in the project Quality Assurance Plan.

The second method of measuring the headspace concentrations of VO used a calibrated total hydrocarbon analyzer. This instrument was a Bacharach TLV Sniffer that pulls a continuous sample that is continuously oxidized by a catalyst-coated resistance element. The resistance of this element varies with temperature, which is in turn proportional to the hydrocarbon concentration of the analyzed gas. For headspace concentration measurement, the sample probe of the sniffer was inserted into the half-filled sample jars, headspace sample was pulled into the analyzer, and the resulting maximum measured concentration recorded as the headspace concentration of VO for the sample. These readings gave the total hydrocarbon concentration of the headspace gases, expressed as parts per million hexane. These measurement were intended

to be a rough measurement of headspace concentrations and to confirm the results from GC analysis of headspace concentrations. The Bacharach TLV Sniffer had a maximum measurable concentration of 10,000 ppm and this range was exceeded by all of the headspace samples of the feed samples. Although unable to measure the actual headspace concentration of these samples, the sniffer did give a qualitative measurement of the concentrations (greater than 10,000 ppm).

The Bacharach TLV was also used to measure concentrations of organics in the vent gas, feed tank headspace, and vapors above the bottoms when the sample pot was removed from the TFE. Measured organic concentration of the vent gas and feed tank headspace also exceeded the range of the instrument.

A wet test meter was used to measure the vent gas flow rate from the primary condenser. This instrument (Precision Scientific catalog No. G3115) is considered a primary standard for the measurement of relatively small flow rates and was attached directly to the vent gas outlet. Measurements of the vent gas flow rate were taken only when no diversion of the vent gas (i.e., through the condenser condensate sample line) was occurring.

Volatile Analyses by CompuChem

The volatile samples were prepared for analysis according to the EPA Contract Laboratory Program (CLP) protocols for volatile analyses. Sample Luwa 168 was analyzed by purging 175 µL. The liquid oil samples, LUWA 149, 156, 164, and 172, were diluted 1:1,000 with methanol prior to the injection of 1.0 µL into a megabore capillary column. The six sludge samples were analyzed as medium-level methanol extracts. Approximately 4 grams of each sample was extracted with 10 mL of methanol. From 1 to 100 µL of the resulting extract was purged.

All volatile analyses were analyzed within the CLP-specified 12-hour tune timeframe. Quantitations are based on a five-point calibration or verifying shift standard. At the beginning of each 12-hour period, the instrument met all 4-bromofluorobenzene (BFB) tuning criteria specified by the CLP protocols. An acceptable instrument blank was obtained prior to processing the first sample of each tune period. Acceptance criteria for instrument blanks are:

- Methylene chloride, acetone, and toluene levels must be below two times the reported detection limit.
- All compounds other than methylene chloride, acetone, and toluene must be below the reported detection limit.

2-Butanone may be present in medium-level methanol extract blanks at levels of 8 to 15 times the detection limit. This compound is a naturally occurring contaminant in methanol.

Surrogate and internal standards were added to each sample prior to purging. The surrogate compounds used are:

- d4-1,2-Dichloroethane--150 ng

- Bromofluorobenzene--150 ng
- d8-Toluene--150 ng.

The internal standard compounds used are:

- Bromochloromethane--150 ng
- 1,4-Dichlorobenzene--150 ng
- d5-chlorobenzene--150 ng.

The internal standard areas are required to be within -50 and +100 percent of the corresponding area in the shift standard. Failure to meet this criterion requires the repreparation and reanalysis of the sample.

A Finnigan OWA GC/MS equipped with a Tekmar purge and trap device and a 6 ft x 1/4 in. glass column packed with 1 percent SP-1000 on Carbopack B was used for the volatile analysis of the sludge extracts and aqueous condensate. The following temperature program was used:

- Initial temperature--50°
- Initial hold--3 min
- Ramp rate--8°/min
- Final temperature--215°.

The four liquid oil samples required analysis using a Finnigan OWA equipped with a 30-m megabore DB624 column. The following temperature program was used for those analyses:

- Initial temperature--30°
- Ramp rate--8°/min
- Final temperature--260°.

Semivolatile Analyses by CompuChem

The semivolatile samples were prepared for analysis according to the EPA CLP protocols for semivolatile analyses. The water sample was analyzed by extracting 100 mL of liquid with methylene chloride after pH adjustment to greater than 11 and to less than 2 and concentrating the resulting extract to 1.0 mL. The 1.0 g of each oil sample was diluted to 25.0 mL with methylene chloride. The sludge samples were extracted using approximately 30 g of samples. Final extract volumes for the sludge samples ranged from 8.0 to 20 mL.

All semivolatile analyses have been analyzed within the CLP-specified 12-hour tune timeframe. Quantitations are based on a five-point calibration or verifying shift standard. At the beginning of each 12-hour period, the

instrument met all decafluorotriphenyl phosphine (DFTPP) tuning criteria specified by the CLP protocols. Method blanks were prepared and analyzed with each batch of samples. These blanks met the following criteria:

- Phthalate levels must be below two times the reported detection limit.
- All compounds other than the phthalates must be below the reported detection limits.

Surrogate standards were added to each sample (except the oil samples) immediately prior to extraction. The surrogate compounds used are:

- 2-Fluorophenol--100 μg/L
- d5-Phenol--100 μg/L
- d5-Nitrobenzene--50 μg/L
- 2-Fluorobiphenyl--50 μg/L
- 2,4,6-Tribromophenol--100 μg/L
- d14-Terphenyl--50 μg/L
- d10-Pyrene--50 μg/L.

Internal standards were added to extract aliquots immediately prior to analysis. The internal standard compounds used are:

- d4-1,4-Dichlorobenzene--40 ng/μL of extract
- d8-Naphthalene--40 ng/μL of extract
- d10-Acenaphthene--40 ng/μL of extract
- d10-Phenanthrene--40 ng/μL of extract
- d12-Chrysene--40 ng/μL of extract
- d12-Perylene--40 ng/μL of extract.

The internal standard areas are required to be within -50 and +100 percent of the corresponding area in the shift standard. Failure to meet this criterion requires the addition of an internal standard to a new extract aliquot and reanalysis of the sample. Control limits for the surrogates are listed on each sample report page. Failure to meet these control limits requires re-extraction and reanalysis of the sample.

A Finnigan OWA equipped with a 30-ft-wide bore thick-film DB-5 column was used for the semivolatile analysis. The following temperature program was used:

- Initial temperature--30°
- Initial hold--3 min
- Ramp rate--19°/min
- Final temperature--310°.

Sample Notes and Observations

The purpose of this section is to summarize observations made during the processing and analysis of the volatile and semivolatile samples analyzed by Compuchem.

The oil samples were not completely soluble in methanol. The diluted samples were allowed to sit for 48 hours before analysis. At the time of analysis, a small bead of oil was still visible in the dilutions of samples Luwa 164 and 172. These two samples were the oil condensates from the high-temperature runs. They contained substantial amounts of higher boiling hydrocarbons that would not be expected to dissolve in methanol. The volatile hydrocarbons would be dissolved, however, so that the presence of a small amount of insoluble oil would not substantially affect the analysis.

The high background present in the volatile analysis of Luwa 188 has obscured the xylenes. Although xylenes may be present in this sample, a positive identification was not possible. This was a feed sample and had substantially different results than the other feed samples analyzed. The material analyzed was probably an aqueous fraction of the feed that had much lower concentrations of volatiles than the actual feed.

The high toluene and benzene content of sample Luwa 185 (feed sample) required additional analysis for quantitation. A composite report has been issued for this sample. Benzene and toluene values have been reported from purging 1.0 μL of the methanol extract. All other values, detection limits, and tentatively identified compounds have been reported from purging 25 μL of the methanol extract.

Some of the samples contained volatile compounds that were present at low levels in the associated volatile blanks. In each case, the affected analyte has been reported with a "B" footnote beside the affected value. The concentrations found in the corresponding blanks are presented below.

Blank	Associated samples	Compound/concentration
104199	Luwa 59, 68, 78, 168, 185, and 188	Methylene chloride, 500 μg/kg Acetone, 2,300 μg/kg 2-Butanone, 15,000 μg/kg Chlorobenzene, 400 μg/kg

Blank	Associated samples	Compound/concentration
104735	Luwa 96	Methylene chloride, 450 µg/kg Acetone, 1,900 µg/kg 2-Butanone, 11,000 µg/kg Toluene, 275 µg/kg Chlorobenzene, 440 µg/kg

None of these compounds (except toluene) was found in significant quantities in the analyzed sludges and condensates. Only toluene was listed in the analytical data compilations, and it was generally present at much greater concentrations than the level found in the blanks.

Inorganic Analyses

Four samples were analyzed for metals following the EPA CLP by Compuchem. The three solid samples were digested and brought to a 100-mL final volume. This then was analyzed by inductively coupled plasma (aluminum, antimony, arsenic, beryllium, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, nickel, silver, sodium, vanadium, and zinc), furnace atomic absorption (barium, selenium, and thallium), flame atomic absorption (potassium), and cold vapor atomic absorption (mercury). All analytical equipment was initially calibrated and verified with continuing calibration samples. Both soil and water matrix blanks were run prior to analysis, an ICAP interference check sample was analyzed, and spiked samples using one sludge sample (Luwa-96) and the aqueous condensate (Luwa-172) were prepared and analyzed. Duplicates and spiked samples for both a sludge sample (Luwa-185) and the aqueous condensate were prepared and analyzed. Serial dilutions (1:4) were performed on the Luwa-188 sample to verify measured values.

GC and GC/MS Analysis of Volatiles at IEA

IEA analyzed the VO concentrations of six gas canisters by GC with a flame-ionization detector, two canisters by GC/MS, and the vapor headspace of two feed sludge samples by GC/MS. This was done to identify the major compounds in the condenser vent gas, their approximate concentrations, and the VO in the feed headspace. The conditions for the GC/FID analysis are:

- Column--3 ft x 1/8 in. SS column packed with 0.19 percent picric acid on Carbopack B
- Initial temperature--50°
- Initial hold--6 min
- Ramp rate--6°/min
- Final temperature--110°
- Standard--Supelco C1 to C6 hydrocarbon standard.

The data obtained by this procedure are quantitative and indicate the relative amounts of VOs found in the condenser vent gas. Because of the relatively large number of peaks found in this GC analysis, it was not possible to identify individual compounds in the vent gas. These samples were not analyzed by GC/MS because of the very low vent gas flow rates observed during the TFE tests; it is not possible to estimate vent gas emissions accurately from the process.

The GC/MS analysis of vent gas canisters and feed headspace was intended both to identify the specific compounds in these samples and to measure their concentrations. The GC/MS analysis of the feed headspace samples was very important in that these analyses confirmed the compound identification of VOs identified by retention times during the onsite GC/FID analysis of the samples. The analytical conditions for the GC/MS analysis of feed headspace and vent gas canisters are:

- Instrument--Finnigan OWA GC/MS/DS
- Column--3 ft x 1/8 in. SS column packed with 0.19 percent picric acid on Carbopack B
- Initial temperature--45°
- Initial hold--3 min
- Ramp rate--8°/min
- Final temperature--220°
- Final time--15 min
- Standard--Purge and trap of 10 mL of 100-ng/mL benzene standard.

Duplicate GC/MS analysis of the one vent gas sample (Luwa-98) was performed. The analysis of two feed headspaces also constituted a duplicate sample analysis.

Water and Solids Analysis

IEA performed oil, water, and solids analysis on 15 samples from the Luwa testing. The oil analysis was performed by standard method No. 413.2 (Freon extraction followed by spectrophotometric measurement of the oil content), water analysis by ASTM D1744 (Karl Fisher titration), and solids analysis by a slightly modified Method 224G for solid and semisolid samples.

ANALYTICAL PROCEDURES FOR PLANT I

Samples for volatile and extractable organics initially screened for volatiles and semivolatiles by gas chromatography/mass spectroscopy (GC/MS). After the individual compounds were identified by GC/MS, the compounds were quantified by EPA Method 601. Method 601 is a purge-and-trap procedure that is used for analysis of purgeable halocarbons by gas chromatography (GC). The

VO data for water in this report are reported for the Method 601 results. The level of VO in the organic phase was determined by direct-injection GC. All of the vapor samples were analyzed by GC with calibration standards for the components of interest. The level of VO in the sludge sample was quantified by EPA Method 5030 (methanol and water extraction followed by purge and trap). EPA's TCLP also was performed on the sludge. Additional details on the analytical procedures can be found in Section 4 of the site-specific test and QA plan dated September 12, 1986.

Several laboratories participated in the analyses because they offered different areas of experience and expertise. Industrial and Environmental Analysts, Inc. (IEA) performed the VO analysis of the sludge. Alliance Technologies Corporation (formerly GCA) performed the TCLP analysis of the sludge. Vapor samples were analyzed at Research Triangle Institute (RTI). Liquid samples of the wastewater and organic phases comprised the vast majority of the analyses conducted. This major analytical effort was provided by EPA's contract laboratory, Engineering and Economics Research, Inc. (EER). EER also performed the analysis of headspace, metals, and solids contents.

ANALYTICAL PROCEDURES FOR PLANT H

The samples for volatile organics in water were analyzed by modified EPA Method 624 (40 CFR Part 136, October 26, 1984). Method 624 is a purge and trap procedure with separation and quantification provided by gas chromatography/mass spectroscopy (GC/MS). This method is particularly well-suited for analysis of ppb levels of the volatile organic compounds and provides a nominal detection limit of 10 ppb. The concentrations of the VO compounds in the stripper feed, aqueous condensate, and effluent spanned several orders of magnitude. Multiple GC/MS runs were required for each sample at various levels of dilution to quantify both the high level and low level constituents. The organic phase of the condensate was analyzed by direct injection gas chromatography and calibration standards of the components of interest. Additional details on analytical procedures can be found in Section 4 of the site-specific test and quality assurance plan dated July 7, 1986.

Tracer gas samples were analyzed by injection of 0.5 cc into a gas chromatograph equipped with a 6 foot by 1/8 inch OD stainless steel column packed with 3 percent SP-1500 on 80/120 mesh Carbopack B and a flame ionization detector. The column temperature was held at 28 °C until propane eluted and then increased to 150 °C to elute the remaining components of the vapor.

The FID response was calibrated by injection of 0.5 cc of 98.5 ppm propane in nitrogen mixed with 0.5 cc of overhead vapor sample (no tracer gas present). Such a mixture was used to provide consistent measurement of the propane peak area since there was some overlap between the propane peak and one of the vapor component peaks. The FID response was recorded on strip chart and the propane peak area was determined by electronic integration. Selected samples were analyzed by Plant H's laboratory to corroborate our analyses.

ANALYSIS PROCEDURES FOR PLANT G

The analyses that were carried out on the process samples are outlined below. Details of the analytical procedures are presented in the Site Specific Test and QA Plan Addendum (RTI, 1984).

Onsite Analysis and Measurements

The onsite analyses were limited to (1) determination of hydrocarbon content of the vent gas stream with a Bacharach TLC meter, and (2) measurement of the vent gas flow with a pitot tube flowmeter attached to an inclined manometer.

Offsite Analysis

Analysis of Vent Gas Samples--
The contents of the evacuated stainless steel canister used to sample the vents were analyzed for volatile organics using the headspace GC method.

Analysis of Liquid Samples--
Semivolatile Organics--The semivolatile organics were measured by extracting the collected liquid samples with methylene chloride, and then analyzing the methylene chloride by GC. Confirmation of peak identification was performed by GC/MS.

Determination of Liquid pH--The pH of liquid samples was measured using pH indicator paper.

Determination of Solids Content--The total solids content of the feed liquid was determined using Method 209C.

APPENDIX E

QUALITY ASSURANCE

APPENDIX E

QUALITY ASSURANCE

The quality assurance (QA) program for these tests included a generic QA plan that was submitted to and approved by EPA. In addition, a site-specific test and QA plan for each site tested was submitted to and approved by the EPA Project Officer and Quality Assurance Officer. The QA program included systems and performance audits of the analytical laboratories. In general, the quality assurance objectives for the most critical measurements associated with the treatment system's perfomance were met. The following sections provide additional details on the QA results for each test.

THIN-FILM EVAPORATOR PILOT STUDY

This section documents the specific quality assurance (QA) procedures used in the analytical measurements of samples. The analyses were: (1) GC/MS analysis of volatiles and semivolatiles by CompuChem, (2) metals analysis by CompuChem, (3) onsite analysis of sludge headspace concentrations by GC/FID and using a total hydrocarbon analyzer, (4) vent gas analysis by GC/MS performed by IEA, and (5) oil, water, and solids analysis performed by IEA. The specific QA procedures used for each set of analyses and any results from QA procedures are described below.

GC/MS Analysis of Volatiles by CompuChem

The sludge samples (feed and bottoms) were extracted with methanol, the oil condensate samples were diluted 1:1000 with methanol, and the aqueous condensate was used as a dilute aqueous sample. All analyses were performed within a 12-hour timeframe of instrument tuning. At the beginning of this 12 hours, the instrument met all bromofluorobenzene (BFB) tuning criteria. The quantitations are based on a five-point calibration and/or verifying shift standard. Acceptable instrument blanks were run prior to processing samples.

Three sample surrogates were added to each sample prior to sample preparation and subsequent analysis. Three internal standards were added to the extracted samples just prior to analysis. (The internal standards and surrogates were added directly to the aqueous condensate just prior to analysis.) Internal standard areas were required to be within -50 to +100 percent of the corresponding area of the shift standard (sample surrogate). Deviations from this range would require the repreparation and analysis of the samples. Recoveries of surrogate sample spikes are listed in Table E-1. The average deviation of surrogate recovery was between 13.7 and 17 percent. Because the surrogate was added to samples prior to sample extraction, this deviation should be a measure of the variation associated with the analysis (analytical precision). The extraction of surrogates from the samples into the methanol was fairly high for most of the samples but noticeably lower (between 70 and

TABLE E-1. SURROGATE RECOVERY FROM VOLATILE ANALYSES (COMPUCHEM DATA)

LUWA run # Sample number Sample type	5 LUWA-185 feed, %	5 LUWA-188 feed, %	6 LUWA-68 bottoms, %	7 LUWA-69 bottoms, %	8 LUWA-78 bottoms, %	10 LUWA-96 bottoms, %	10 LUWA-168 eq cond, %	Average deviation of analysis, %	Control range for surrogate analysis, %
Sample prep/analytical	a	a	a	a	a	a	b		
Surrogate recovery									
d4-1,2-Dichloroethane	68	100	86	99	77	77	97	13.7	70-121
Bromofluorobenzene	102	96	79	78	69	69	97	16.4	74-121
d8-Toluene	86	86	81	96	68	68	104	17.0	81-117

[a]Extraction of 4 g of sample (nominal weight) with 10 mL methanol, GC/MS.
[b]Purge and trap of 175 µL sample, GC/MS.

80 percent) for the two bottoms samples from the high-temperature runs (Luwa-96 and Luwa-78). Measuring surrogates added to the oil samples was not possible because of the large dilutions applied to the prepared samples prior to analysis. This was unfortunate but not catastrophic, as the volatile removal from the sludge was based on analyses of the feed and bottoms samples only.

GC/MS Analysis of Semivolatiles

Samples were prepared for analysis as described in the analytical section of this report. All samples were prepared as extracts (or dilutions with the oil samples) in methylene chloride. Seven surrogate semivolatile compounds were added to the extracted samples prior to extraction of the samples with methylene chloride. No surrogates were added to the diluted oil samples. Six internal standards were added to the extracts just prior to analysis. The instrument met all DFTPP tuning criteria at the beginning of the 12-hour period when the samples were analyzed. Sample quantitation was based on a five-point calibration and/or verifying shift standard. A method blank was prepared and analyzed with the batch of samples.

Of the samples analyzed for semivolatiles, the surrogates were only measured in a single sample, the aqueous condensate extract. The other extracted samples were diluted below the detection limits of the surrogates after extraction. This permitted the major components to be analyzed, but does not allow any assessment to be made of the extractions and sample preparation. The surrogate recovery for the aqueous condensate sample is listed in Table E-2. This sample showed recoveries of between 47 and 93 percent. It is unfortunate that surrogates were not measured in the feed and bottoms samples. If they were, there might be a trend showing less extraction of the surrogate compounds from the bottoms samples than in the feed samples, which would explain the bias observed in the process mass balances using these results. If time and budget had permitted, the samples could have been reanalyzed using both spiked samples (spikes of the actual compounds of interest) and surrogate spikes. As this project was primarily directed to documenting the removal of VOs from the tested sludge, and the concentrations of the semivolatiles would be expected to change drastically with whatever sludge is treated, these results are probably adequate for the project.

Analysis of Metals

Four samples were analyzed for metals following the EPA CLP (Contract Lab Protocol) by COMPUCHEM. The three solid samples were digested and brought to a 100-mL final volume. This was then analyzed by inductively coupled plasma (aluminum, antimony, arsenic, beryllium, cadmium, calcium, chromium, cobalt, copper, iron, lead, manganese, nickel, silver, sodium, vanadium, and zinc), furnace atomic absorption (barium, selenium, and thallium), flame atomic absorption (potassium), and cold vapor atomic absorption (mercury). All analytical equipment was initially calibrated and verified with continuing calibrations samples. Both soil and water matrix blanks were run prior to analysis, an ICAP interference check sample was analyzed, and spiked samples using one sludge sample (Luwa-96) and the organic condensate (Luwa-172) were prepared and analyzed. Duplicates and spiked samples for both a sludge sample

TABLE E-2. SURROGATE RECOVERY DURING SEMIVOLATILE ANALYSIS (COMPUCHEM DATA)

LUWA run #			5	5	7	7	8	8	10	10	10
Sample number	LUWA-185	LUWA-188	LUWA-68	LUWA-149	LUWA-59	LUWA-156	LUWA-78	LUWA-164	LUWA-96	LUWA-172	LUWA-168
Sample type	feed mg/kg	feed mg/kg	bottoms mg/kg	org cond mg/kg	bottoms mg/kg	org cond mg/kg	bottoms mg/kg	org cond mg/kg	bottoms mg/kg	org cond mg/kg	aq cond mg/kg
Sample prep/analytical	a	a	a	b	a	b	a	b	a	b	c
Surrogate recovery											
2-Fluorophenol	d	d	d	e	d	e	d	e	d	e	59
d5-Phenol											47
d5-Nitrobenzene											87
2-Fluorobenzene											84
2,4,6-Tribromophenol											88
d14-Terphenyl											93
d10-Pyrene											92

[a]30-g (nominal) samples extracted with methylene chloride, final extract volume 8-10 mL, GC/MS.
[b]1.0 g oil diluted to 25 mL with methylene chloride, GC/MS.
[c]100 mL of sample extracted with methylene chloride at pH >11 and pH <2, extract concentrated to 1.0 mL, GC/MS.
[d]Sample was diluted for analysis, surrogates below detection limits.
[e]Surrogates were not added to diluted oil samples.

(Luwa-185) and the organic condensate were prepared and analyzed. Serial dilutions (1:4) were performed on the Luwa-188 sample to verify measured values.

RTI: Analysis of Feed and Bottoms Headspace Concentrations

The analysis of feed and bottoms sludge headspace by GC with a flame-ionization detector at the test site required a fairly general approach with respect to both the compounds analyzed and the concentration ranges examined. The composition of the feed sludge for testing was not well known prior to the tests. It was a sample of emulsion tank sludge, and its specific composition would vary widely with whatever emulsions were generated and stored in the tank prior to the removal of the sludge from the tank. The onsite analysis was therefore directed toward the analysis of VOs in the vapor headspace, without having to know precisely which compounds were being measured onsite. The specific compounds were determined initially by compound retention times and confirmed later by GC/MS analysis of of the feed headspace.

The samples for headspace analysis of VO compounds were half-filled 500-mL amber bottles, with modified caps to allow gas sample removal through a septum on the bottle's cap. Samples (25 μL) were withdrawn from the bottle and injected into a GC with a flame-ionization detector. It was calibrated with both a C1 to C6 gas hydrocarbon standard (methane, ethane, propane, butane, pentane, and hexane 100 ppm in N_2) and a liquid benzene standard (200 μg/mL). A hexane standard (500 ppm, also used the Bacharach TLV calibration) was injected to verify quantitation of hydrocarbons. Table E-3 shows the results of this standard analysis. Samples of toluene were injected to determine the retention time of the compound. The field analysis was conducted without knowing the specific organic compounds that would be present in the samples. The compound peaks were identified by the retention times of eluting compounds, and the identification was confirmed by GC/MS analysis of headspace samples by IEA. The headspace samples were found to contain propane, butane, pentane, hexane, benzene, and toluene. 2-Butene, cyclopentane, 2-methyl pentane, and 2-methyl butane were also detected in substantial concentrations.

The headspaces of two sets of triplicate feed samples were measured by this procedure. Table E-4 shows the average concentrations measured, the standard deviation of the measurements, and the percent relative standard deviation (RSD) of the six measurements. The percent RSD was below 10 percent for all components except for the most volatile (propane) and toluene. The toluene peaks eluted relatively late and had some peak broadening that would increase the errors associated with area measurement. The percent RSDs in this table are a measure of the precision of the procedure while the hexane standard was a measure of its accuracy. Table E-5 shows the results of a duplicate sample injection of feed sludge headspace. The percent differences between the two injections are generally smaller than the percent RSDs in Table E-4, but display the same trends with respect to propane and toluene concentrations.

The second method of measuring the headspace concentrations of VOs uses a calibrated total hydrocarbon analyzer. This instrument was a Bacharach TLV Sniffer, which pulls a continuous sample that is continuously oxidized by a

TABLE E-3. HEXANE STANDARD ANALYSIS[a]

Compound	Concentrations		% Difference
	Actual, µg/mL	Measured, µg/mL	
Hexane	1.92	1.79	7.4

[a]Used 500 p/m hexane standard in nitrogen (±5%).

TABLE E-4. RELATIVE STANDARD DEVIATION OF ONSITE GC/FID ANALYSES[a]

Compound	Average concentration, µg/L	Standard deviation	% Relative standard deviation
Propane	121	20	16
Butane	1,065	55	5
2-Methylbutane	1,138	66	6
Pentane	1,029	79	8
2-Methylpentane	421	36	9
Benzene	1,516	105	7
Hexane	432	36	8
Toluene	1,143	277	24

[a]Results from six analyses of feed headspace concentrations, from triplicate samples of feed sludge from runs 5, 6, and 7 (feed drum #3) and runs 8, 9, and 10 (feed drum #4).

TABLE E-5. DUPLICATE SAMPLE INJECTION, FEED DRUM NO. 3

Compound	Concentrations μg/mL	μg/mL	% Difference
Propane	102	136	28.5
Butane	1,019	1,076	5.4
2-Methylbutane	1,158	1,202	3.8
Pentane	1,000	1,019	1.9
2-Methylpentane	423	392	7.6
Benzene	1,519	1,434	5.8
Hexane	435	413	5.2
Toluene	1,588	1,033	42.3

catalyst-coated resistance element. The resistance of this element varies with temperature, which is in turn proportional to the hydrocarbon concentration of the analyzed gas. The instrument was calibrated with a 500-ppm hexane standard immediately prior to the analysis of samples. For headspace concentration measurement, the sample probe of the sniffer was inserted into the half-filled sample jars, the headspace sample was pulled into the analyzer, and the resulting maximum measured concentration was recorded as the headspace concentration of VOs for the sample. These readings gave the total hydrocarbon concentration of the headspace gases, expressed as parts per million hexane. These measurements were intended to be a rough measurement of headspace concentrations and to confirm the results from GC analysis of headspace concentrations. All of the samples for concentration measurement were mixed randomly, and the analysis of all the samples took only about 15 minutes. The results of a triplicate sample (run 5) and three duplicate samples are presented in Table E-6. This shows that the technique was fairly reproducible, although no specific measurements of the unit's accuracy were made during the testing. The Bacharach TLV Sniffer had a maximum measurable concentration of 10,000 ppm and its range was exceeded by all of the headspace samples of the feed samples. Although unable to measure the actual headspace concentration of these samples, the sniffer did give a qualitative measurement of the concentrations (greater than 10,000 ppm). The calibration of the Bacharach TLV was checked using the 500 ppm hexane standard immediately after the analyses were completed to verify that the instrument did not drift significantly. This showed a drift of less than 5 percent during the course of the measurements.

The Bacharach TLV was also used to measure concentrations of organics in the vent gas, feed tank headspace, and vapors above the bottoms when the sample pot was removed from the TFE. Measured organic concentration of the vent gas and feed tank headspace also exceeded the range of the instrument.

IEA: Oil, Water, Solids, GC, and GC/MS Analysis of Vent Gas Concentrations

An attempt was made to perform oil, water, and solids analysis of selected feed sludge, bottoms, organic condensate, and aqueous condensate samples. The oil analysis was performed by Standard Method No. 413.2 (Freon extraction followed by spectrophotometric measurement of the oil content), water analysis by ASTM D1744 (Karl Fisher titration), and solids analysis by a slightly modified method 224G for solid and semisolid samples. For both the oil analysis (by Freon extraction) and the solids (by Method 244G), the amount of residue or oil measured is actually defined by the procedure itself (e.g., the amount of Freon-extractable oil is the amount of oil extracted by this procedure). The procedures were applied in a qualitative manner to the samples, and the results should be viewed as relative applications of the procedures. There were no specific procedures to assess the data quality of these procedures, with the exception of duplicate sample analyses. The results of the duplicate oil, water, and solids analyses are presented in Table E-7.

IEA analyzed the VO concentrations of six gas canisters by GC with a flame-ionization detector, two canisters by GC/MS, and the vapor headspace of two feed sludge samples by GC/MS. This was to identify the major compounds in

TABLE E-6. BACHARACH TLV DUPLICATE MEASUREMENTS OF TOTAL HYDROCARBON IN SAMPLE HEADSPACE

Sample No.	Run No.	Headspace concentration (p/m hexane)[a]
LUWA-47	5	82
LUWA-65	5	78
LUWA-66	5	81
Run #5 Average		80
Run #5 Standard Dev		1.7
Run #5 %RSD		2.1%
LUWA-56	7	120
LUWA-57	7	120
Run #7 Average		120
Run #7 %Difference		0.0%
LUWA-75	8	83
LUWA-76	8	72
Run #8 Average		77.5
Run #8 %Difference		14.2%
LUWA-93	10	32
LUWA-94	10	23
Run #8 Average		27.5
Run #8 %Difference		32.7%

[a]Measurements taken at 25 °C.

TABLE E-7. OIL, WATER, AND SOLIDS ANALYSIS, PERCENT DIFFERENCE OF DUPLICATE SAMPLE

	Feed drum #4 LUWA-83	Feed drum #4 LUWA-83D	Average	% Difference
Residue 105 °C	36.6%	34.4%	35.5%	6.2
Residue 300 °C	3.4%	5.7%	4.6%	50.5
Residue 550 °C	1.8%	1.8%	1.8%	0.0
Oil (g/L)	850	840	845	1.2
Water (weight %)	59.00%	59.00%	59.00%	0.0

the condenser vent gas, their approximate concentrations, and the VOs in the feed headspace.

The GC data on the vent gas concentration used only a C1 to C6 hydrocarbon standard for calibration and then grouped the eluting compounds into C1, C2, C3, C4, C5, C6, and C7 ranges to which the appropriate response factor was applied for the entire range. The data obtained by this procedure are quantitative and indicate the relative amounts of VOs found in the condenser vent gas. Because of the relatively large number of peaks found in this GC analysis, it was not possible to identify individual compounds in the vent gas. These samples were not analyzed by GC/MS because of the wide variation of results expected and the very low vent gas flow rates observed during the TFE tests. It would not have been possible to estimate accurately vent gas emissions from the process even if there were an excellent analysis of the samples, so this less expensive and qualitative approach was used instead. This procedure was not audited, and the two duplicate samples analyzed (run 8, Luwa-84, and Luwa-85) show exceptionally poor reproducibility.

The GC/MS analysis of vent gas canisters and feed headspace was intended both to identify the specific compounds in these samples and to measure their concentrations. The GC/MS analysis of the feed headspace samples was very important in that these analyses confirmed the compound identification of VOs identified by retention times during the onsite GC/FID analysis of the samples. The analytical conditions for this analysis are contained in Section 5 of this report. A single 100-ng/mL benzene standard was used to calibrate the analytical method. Although the quality of these data is substantially below that produced by CompuChem, the identification of specific compounds is probably very accurate.

Duplicate GC/MS analysis of the one vent gas sample (Luwa-98) was performed. The analysis of two feed headspaces also constituted a duplicate sample analysis. These results, and the calculated percent differences, are shown in Table E-8.

QUALITY ASSURANCE FOR PLANT I

The QA program for this test is described in the site-specific test and QA plan dated September 12, 1986. In addition, an audit of the field sampling activities was conducted for EPA by an independent contractor (S-Cubed). No significant problems were found in the audit.

The QA goals for this test are summarized in Table E-9. The results of the number of samples planned and those successfully analyzed are given in Table E-10.

Accuracy results for VO in water are presented in Table E-11 and show a percent recovery of 90 to 117 percent or a percent bias of -10 to 17 percent. A total of nine samples were spiked with the target to evaluate the effects of the sample matrix on percent recovery. Precision results for the stripper feed and bottoms are presented in Tables E-12 and E-13, respectively. The various replicate samples were taken sequentially in the field and submitted blind to the laboratory; consequently, the precision results represent the

TABLE E-8. % DIFFERENCE, GC/MS ANALYSIS OF GAS SAMPLES, VENT GAS AND HEADSPACE (IEA)

Compound	Vent gas run #10 LUWA-98, µg/L	Vent gas run #10 LUWA-98, µg/L	% Difference vent gas run #10	Feed headspace drum #3 LUWA-44, µg/L	Feed headspace drum #4 LUWA-81, µg/L	% Difference feed headspace
2-Methyl propane					1,800	
Butane	2,800	2,600	7	2,200	3,800	53
2-Butene				890	1,400	45
Cyclopentane				870	1,000	14
2-Methyl butane	6,000	4,800	22	4,500	6,300	33
Pentane	8,800	6,800	26	6,300	8,300	27
2-Methyl-1-pentene		1,200				
Methyl cyclopentane	2,300	1,700	30	1,600	1,900	17
3-Methyl pentane	2,500	1,800	33			
2-Methyl pentane	6,300	4,400	36	4,300	5,000	15
Benzene	3,000	2,000	40	1,800	2,000	11
Hexane	3,900	2,500	44	2,300	2,600	12
Methyl cyclohexane	1,500	1,000	40	1,000		
3-Methyl hexane	1,400					
Toluene	10,000	7,200	33	7,600	8,000	5

TABLE E-9. PRECISION, ACCURACY, AND COMPLETENESS OBJECTIVES

Parameter	Precision (% RSD)[a]	Accuracy (% Bias)	Completeness (%)
Volatile organics	25	25	90
Extractable organics	25	25	90
Metals	15	20	95
Dissolved solids	20	b	100
Filterable solids	20	b	100

[a]RSD = relative standard deviation.

[b]The method states that there is no satisfactory procedure to obtain a measure of accuracy.

TABLE E-10. PERCENT COMPLETENESS RESULTS

	Location	Type	Number of samples Planned	Number of samples Analyzed	Percent completed
S1	Water to decanter	Volatile organics	13	5	38[a]
		Solids	4	2	50[a]
		Metals	4	3	75[a]
		Headspace	2	1	50[a]
S2	Organic phase	Volatile organics	6	5	83
		Headspace	2	2	100
		Solids	2	1	50
S3	Sludge	Volatile organics	7	7	100
		Solids	4	4	100
		Headspace	2	1	50
		TCLP	4	4	100
S4	Water from decanter	Volatile organics	6	8	133[b]
		Solids	4	5	125[b]
		Headspace	2	3	150[b]
		Metals	0	2	--
S5	Stripper feed	Volatile organics	13	15	115
		Headspace	4	2	50
		Solids	4	2	50[c]
		Metals	5	5	100
S6	Stripper bottoms	Volatile organics	13	15	115
		Solids	2	3	150[c]
		Headspace	2	2	100
S7	Organic condensate	Volatile organics	12	12	100
		Headspace	2	2	100
S8	Primary condenser	Volatile organics	8	8	100
S9	Secondary condenser	Volatile organics	8	8	100
S10	Storage tank	Volatile organics	6	6	100
S11	Condensate tank	Volatile organics	4	2	50[d]
S12	Decanter	Volatile organics	4	3	75[d]

[a]The number of samples taken at S1 were decreased because flow occurred at S1 into the decanter on only one test day. Because of no flow on the second test day, the number of samples at S5 and S6 was increased.

[b]The number of samples taken at S4 was increased to assess concentrations before and after treatment in the decanter.

[c]The replicate analysis for soids was performed on S6 instead of S5.

[d]The number of vapor canister samples was reduced because of inadequate vacuum on several vapor canisters before sampling.

TABLE E-11. ACCURACY RESULTS FROM MATRIX SPIKES OF VOLATILE ORGANICS IN WATER[a]

Compound	Number of samples	Average recovery (percent)	Standard deviation
Chloromethane	9	96.1	13.6
Methylene chloride	9	117	9.4
1,1-Dichloroethene	9	90.4	10.2
Chloroform	9	94.5	0.25
1,2-Dichloroethane	9	103	12.6
Carbon tetrachloride	9	97.0	8.6
Trichloroethene	9	91.5	7.0
1,1,2-Trichloroethane	9	96.7	9.3

[a]Spike levels ranged from 7 to 125 ppb.

TABLE E-12. PRECISION RESULTS FOR VOLATILE ORGANICS IN STRIPPER FEED (S5)

Compound	Replicates (ppm)				Relative standard deviation (percent)
	1	2	3	4	
Chloromethane	31.1	19.2	26.3	24.6	19
Methylene chloride	3,680	3,505	4,072	2,899	14
Chloroform	1,227	1,164	784	2,090	42
Carbon tetrachloride	67.7	54.8	45.4	65.3	18
Trichloroethylene	5.4	6.2	10.2	0	77

TABLE E-13. PRECISION RESULTS FOR VOLATILE ORGANICS IN STRIPPER BOTTOMS (S6)

Compound	Replicates (ppm)				Relative standard deviation (percent)
	1	2	3	4	
Chloromethane	<0.005	<0.005	<0.005	<0.005	0
Methylene chloride	33.3	16.8	8.4	9.4	68
Chloroform	<0.005	<0.005	<0.005	<0.005	0
Carbon tetrachloride	<0.005	<0.005	<0.005	<0.005	0
Trichloroethylene	<0.005	<0.005	<0.005	<0.005	0

overall precision and include variations in the process over the sampling time, sampling, and analysis. The precision for two of the three major compounds in the feed, methylene chloride and carbon tetrachloride, are within the target goals of 25 percent. The results for chloroform and trichloroethylene are more variable with percent relative standard deviations of 42 and 77 percent, respectively. Precision results for VO components in the wastewater from the solids decanter (S4) are given in Table E-14. These results show reasonable precision for all compounds except carbon tetrachloride. The precision results for the pure organic phase are given in Table E-15. These precision results meet the target goals except for one set of replicates for chloroform (S7).

The percent recovery of VO from the sludge is shown in Table E-16. The target compounds were spiked into the sludge matrix, and the results show a low recovery of the spike for all compounds. Precision results for VO in the sludge are given in Table E-17 and show that the precision goals were met except for carbon tetrachloride. One of these samples had a high reported concentration of carbon tetrachloride (14 percent) compared with two values at 3.7 and 3.8 percent.

The accuracy results for vapor analyses are given in Table E-18. The recoveries were all high; however, each analysis was within the target goals for accuracy. The precision results for the vapor canisters are given in Tables E-19 and E-20. All of these samples also were submitted blind to the laboratory, i.e., the analyst did not know that the samples were replicates. The precision goals were met except for carbon tetrachloride in one set of replicates.

The precision results for metals in the wastewater are summarized in Table E-21 and show reasonable precision except for one low value for chromium and one low value for lead that significantly increased the relative standard deviation. Table E-22 presents the analytical precision for the solids measurements. These samples were split in the laboratory and analyzed as replicates. The overall precision results for solids are given in Table E-23 and include the variations in both sampling and analysis.

The accuracy results for VO in the TCLP extract are given in Table E-24 with reported recoveries of 66 to 84 percent (-16 to -34 percent bias). The precision results in Table E-25 show acceptable agreement among the three replicates. The accuracy results for metals in the TCLP extract are given in Table E-26 and reveal a range of 92 to 106 percent recovery. The precision results for metals in Table E-27 also show a good agreement among the three replicates.

Although some of the data failed to meet the target goals for precision, the data provide a reasonable assessment of the system's performance for removal of VO compounds from the waste. For example, the variations in measured feed and bottoms concentrations do not affect the calculated percent removal for the various compounds. The greatest variability was noted in analyses for carbon tetrachloride, which contributed about 1 percent of the total VO in the feed. The system's performance for total VO removal should be reasonably accurate because of acceptable accuracy and precision data for

TABLE E-14. PRECISION RESULTS FOR VOLATILE ORGANICS FROM SOLIDS DECANTER (S4)[a]

Compound	Replicates (before treatment)			Relative standard deviation (percent)
	1	2	3	
Chloromethane	43.5	29.8	44.7	21
Methylene chloride	4,869	5,576	3,571	22
Chloroform	1,170	1,821	1,920	25
Carbon tetrachloride	310	60.5	82.4	99
1,1,2-Trichloroethane	6.4	8.0	9.7	21

Compound	Replicates (after treatment)			Relative standard deviation (percent)
	1	2	3	
Chloromethane	--	17.5	21.4	--
Methylene chloride	3,970	3,071	4,350	17
Chloroform	1,464	1,967	1,467	18
Carbon tetrachloride	16.8	21.1	45.1	55
1,1,2-Trichloroethane	4.6	6.2	6.9	20

[a]All results in parts per million.

TABLE E-15. PRECISION RESULTS FOR ORGANIC SAMPLES (g/L)

Location	Methylene chloride	Chloroform
Solid decanter (S2)	890	449
	892	387
	917	405
Percent relative standard deviation	1.7	7.7
Condenser decanter (S7)	905	254
	1,040	284
Relative percent difference	14	11
Condenser decanter (S7)	1,300	325
	1,220	469
Relative percent difference	6.3	36

TABLE E-16. ACCURACY RESULTS FOR VOLATILE ORGANICS IN SLUDGE (PERCENT)[a]

Compound	Measured after spiking	Measured before spiking	Spike recovery	Percent recovery of spike[b]
Methylene chloride	9.44	7.58	1.86	58
Chloroform	6.68	4.28	2.40	75
Carbon tetrachloride	5.63	3.72	1.91	60

[a]Spiked into the sludge sample.

[b]Based on a spiked concentration of 3.2 percent.

TABLE E-17. PRECISION RESULTS FOR VOLATILE ORGANICS IN SLUDGE (S3)

Compound	Replicates (percent)			Relative standard deviation
	1	2	3	
Methylene chloride	7.66	7.49	8.93	9.8
Chloroform	4.32	4.23	5.50	15
Carbon tetrachloride	3.66	3.81	14.1	83

Compound	Replicates (percent)		Relative percent difference
	1	2	
Methylene chloride	18.5	20.6	11
Chloroform	9.56	10.0	4.5

TABLE E-18. ACCURACY RESULTS FOR VAPOR ANALYSES (ppm)

Compound	True concentration	Measured values		Percent recovery	
		1	2	1	2
Methylene chloride	6.0	6.0	6.9	100	115
Chloroform	342	348	349	102	102
Carbon tetrachloride	20.8	23.3	21.0	112	101

TABLE E-19. PRECISION RESULTS FOR VAPOR ANALYSES AT S8

Compound	Replicates (percent)			Relative standard deviation (percent)
	1	2	3	
Chloromethane	0.63	0.62	0.63	0.9
Methylene chloride	39.16	38.71	38.79	0.6
Chloroform	3.99	3.88	3.91	1.4
Carbon tetrachloride	0.192	0.168	0.179	6.7

TABLE E-20. PRECISION RESULTS FOR VAPOR ANALYSES AT S9

Compound	Replicates (percent)			Relative standard deviation (percent)
	1	2	3	
Chloromethane	0.59	0.58	0.45	14
Methylene chloride	38.16	38.52	31.55	11
Chloroform	4.41	4.13	3.21	16
Carbon tetrachloride	0.575	0.324	0.209	51

TABLE E-21. PRECISION RESULTS FOR METALS IN STRIPPER FEED (S5)
(ppb unless otherwise noted)

Metal	Replicates			Relative standard deviation (percent)
	1	2	3	
Arsenic	<1.0	<1.0	<1.0	0
Beryllium	0.57	0.52	0.46	10.7
Cadmium	8.76	8.49	6.89	12.6
Chromium	0.80	3.46	3.10	59
Copper	70.6	69.6	78.2	6.5
Mercury	[a]	[a]	[a]	[a]
Nickel[b]	1.55	1.89	1.74	9.8
Lead	2.62	0.26	3.80	81
Selenium	<2.0	<2.0	<2.0	0
Zinc[b]	0.25	0.26	0.26	2.2

[a]Not detected at an absolute detection limit of 4 ng.
[b]Results for nickel and zinc are in parts per million.

TABLE E-22. ANALYTICAL PRECISION FOR SOLIDS

Analysis	Location	Replicates 1	Replicates 2	Relative percent difference
Dissolved (percent)	S6	0.42	0.41	2.4
	S4	2.27	1.76	25
	S4	1.18	1.14	3.4
Filterable (ppm)	S6	11	8.0	32
	S4	51	40	24
	S4	1,126	1,032	8.7
Total (percent)	S1	2.38	2.33	2.1

TABLE E-23. OVERALL PRECISION RESULTS FOR SOLIDS ANALYSES

Analysis	Location	Replicates 1	2	3	Relative standard deviation (percent)
Dissolved (percent)	S4	5.05	4.32	4.15	11
	S4	2.01	1.66	1.61	12
	S5	0.47	0.46	0.46	1.2
Filterable (ppm)	S4	48	56	48	9.1
	S4	8.0	8.0	16	43
	S5	51	40	64	23
Total (percent)	S3	11.1	13.1	11.9	8.4
	S1	2.38	2.33	2.53	4.3

TABLE E-24. ACCURACY RESULTS FOR TCLP VOLATILE ORGANICS ANALYSIS OF SLUDGE

Compound	Expected[a] (ppm)	Measured (ppm)	Percent recovery
Carbon tetrachloride	10	6.6	66
Chloroform	10	7.8	78
Methylene chloride	10	8.4	84

[a]Spiked into the extraction blank.

TABLE E-25. PRECISION RESULTS FOR TCLP VOLATILE ORGANICS ANALYSIS OF SLUDGE (S3)

Compound	Replicates (ppm)			Relative standard deviation (percent)
	1	2	3	
Carbon tetrachloride	220	210	210	2.7
Chloroform	2,500	2,600	2,600	2.2
Methylene chloride	7,100	6,600	7,500	9.0

TABLE E-26. ACCURACY RESULTS FOR TCLP METALS ANALYSIS OF SLUDGE (S3)

Metal	Expected[a] (ppm)	Measured (ppm)	Percent recovery
Arsenic	0.50	0.52	104
Barium	1.12	1.03	92
Cadmium	0.681	0.661	97
Chromium	0.603	0.597	99
Lead	0.50	0.52	104
Mercury	0.0055	0.0053	96
Selenium	0.50	0.53	106
Silver	0.50	0.46	92

[a]Based on original analysis plus known amount spiked into sample.

TABLE E-27. PRECISION RESULTS FOR TCLP METALS ANALYSIS OF SLUDGE (S3)

Metal	Replicates (ppm)			Relative standard deviation (percent)
	1	2	3	
Arsenic	<0.04	<0.04	<0.04	0
Barium	0.57	0.63	0.57	5.6
Beryllium	0.003	0.003	0.003	0
Cadmium	0.180	0.180	0.174	1.9
Chromium	0.113	0.106	0.102	5.2
Copper	0.368	0.334	0.334	5.7
Iron	11.1	11.0	9.1	11
Lead	<0.02	<0.02	<0.02	0
Mercury	0.0006	0.0005	0.0005	11
Nickel	58.4	59.5	60.4	1.7
Zinc	36.5	37.9	34.2	5.2

methylene chloride, which was the major component in the feed (77 percent of the total VO).

QUALITY ASSURANCE FOR PLANT H

The quality assurance program for this test is described in the site-specific test and quality assurance plan dated July 7, 1986. A complete technical systems audit of the analytical laboratory (IEA, Inc.) was conducted on July 10, 1986, by RTI and a final audit report was issued on August 12, 1986. The laboratory was rated "acceptable" in this audit report.

The quality assurance goals for this test are summarized in Table E-28. The results of the number of samples planned and those successfully analyzed (percent completeness) are given in Table E-29.

Two types of performance samples were used to assess the accuracy of analysis of volatile organics in water. One sample was spiked with a high level of 1,2-dichloroethane to simulate levels expected in the stripper influent, and another sample was spiked at lower levels to assess the accuracy of chlorinated organic compounds found at levels lower than 1,2-dichloroethane. Both types of samples were submitted as unknowns (constituents and concentrations were not given to the analyst) to the analytical laboratory for analysis and the results are given in Table E-30. Recovery of methylene chloride was high (+39 percent bias) and exceeded the goal of ± 20 percent. Precision was assessed for volatile organics in water by the analysis of triplicate samples taken sequentially from the influent (high levels) and effluent (low levels). The precision results are summarized in Table E-31.

The accuracy of analysis of volatile organic compounds in the vapor phase was assessed by the analysis of the constituents of interest in audit gas cylinders (Table E-32). These results show low percent recoveries for 1,2-dichloroethane and 1,1-dichloroethene. The actual results for 1,2-dichloroethane from the vapor canisters are not expected to be low by a factor of ten. The vapor pressure of pure 1,2-dichloroethane at 2 to 10 °C is 23 to 62 mm Hg. The vapor phase concentration for the pure compound based on this vapor pressure is 130 to 205 mg/L. Most of the vapor canisters were reported to contain around 160 mg/L of 1,2-dichloroethane; consequently, the reported results could not be low by an order of magnitude. Calibration or calculation errors on the analysis of audit cylinders were suspected, but no problems were found. The data from the vapor-phase analyses are considered suspect and affect the estimates of condenser vent rate and efficiency. Precision was assessed by the analysis of triplicate vapor canister samples taken sequentially from the condenser vent (Table E-33). The goal of 25 percent was exceeded for all compounds except the major constituent (1,2-dichloroethane).

Accuracy for metals analysis was evaluated by matrix spiking of the major metals found in the analysis with the results given in Table E-34. Precision was assessed by the analysis of triplicate samples with results shown in Table E-35. Precision results for filterable and dissolved solids are given in Table E-36.

TABLE E-28. QUALITY ASSURANCE GOALS

Parameter	Precision (% RSD)[a]	Accuracy (% Bias)	Completeness (%)
Volatile organic compounds (in liquid phase)	25	20	90
Volatile organic compounds (in vapor phase)	25	20	90
Metals	15	20	95
Dissolved solids	20[b]	b	100
Filterable solids	20[b]	b	100

[a]RSD = Relative standard deviation.

[b]The method states that there is no satisfactory procedure to obtain accuracy because the true concentration is not known. The precision of 20 percent represents our goal for this effort; however, the method states that precision data are not available.

TABLE E-29. COMPLETENESS RESULTS

Sample Type	Number Planned	Number Collected and Analyzed	Percent Completeness
Volatile organics (influent)	14	14	100
Volatile organics (effluent)	14	14	100
Volatile organics (condensate)	12	20[a]	167[a]
Headspace	8	4[b]	50
Volatile organics (vapor canisters)	14	14	100
Filterable solids	6	6	100
Dissolved solids	6	6	100
Metals	6	6	100

[a]Number of samples increased during the test to provide separate samples for organic and aqueous phases.

[b]One sample broken in shipment and triplicates were missed.

TABLE E-30. ACCURACY RESULTS FOR VOLATILE ORGANICS

Compound	Spiked Concentration (mg/L)	Measured Concentration (mg/L)	Percent Bias
1,2-Dichloroethane	102,000	110,000	+7.8
Benzene	442	470	+6.3
Chloroform	5,380	5,000	-7.1
Methylene chloride	1,008	1,400	+39

TABLE E-31. PRECISION RESULTS FOR VOLATILE ORGANICS (mg/L)

Compound	Influent			% RSD	Effluent			% RSD
	No. 1	No. 2	No. 3		No. 1	No. 2	No. 3	
1,2-Dichloroethane	4,700	4,500	4,700	2.5	.22	.20	.18	10
Chloroform	240	230	260	6.3	.56	.61	.62	5.4
Benzene	<.2	<.2	<.2	0.0	<.01	<.01	<.01	0
Carbon tetrachloride	2.4	1.2	1.7	34	<.01	<.01	<.01	0
Chlorobenzene	.28	.24	.22	12	<.01	<.01	<.01	0
Chloroethane	6.8	5.7	3.3	34	<.01	<.01	<.01	0
1,1-Dichloroethane	8.4	7.1	7.8	8.4	<.01	<.01	<.01	0
1,1-Dichloroethene	2.7	2.3	1.2	38	<.01	<.01	<.01	0
1,2-Dichloroethene	5.4	4.9	5.2	4.9	<.01	<.01	<.01	0
Methylene chloride	1.6	1.1	1.1	23	<.01	<.01	<.01	0
Tetrachloroethene	0.80	.74	0.70	6.7	<.01	<.01	<.01	0
1,1,2-Trichloroethane	6.7	5.8	5.4	11	<.01	<.01	<.01	0
Trichloroethene	3.2	2.8	2.7	9.1	<.01	<.01	<.01	0
Vinyl chloride	7.9	6.3	6.9	11	<.01	<.01	<.01	0

TABLE E-32. ACCURACY RESULTS FOR AUDIT GAS CYLINDERS

Compound	Cylinder A			Cylinder B			Cylinder C		
	Reported (ppm)	True (ppm)	Percent Bias	Reported (ppm)	True (ppm)	Percent Bias	Reported (ppm)	True (ppm)	Percent Bias
1,2-Dichloroethane	9.5	97	-90	---	---	---	---	---	---
1,1-Dichloroethene	---	---	---	8.47	15.2	-44	---	---	---
Vinyl chloride	---	---	---	---	---	---	5.78	6.1	-5.2

TABLE E-33. PRECISION RESULTS FOR VAPOR CANISTERS (mg/L)[a]

Compound	No. 1	No. 2	No. 3	% RSD[b]	RPD[c] (No. 2 and 3)
Vinyl chloride	26	61	64	42	4.8
Chloroethane	14	28	31	37	10
1,1-Dichloroethene	7.9	23	29	54	23
1,1-Dichloroethane	4.2	9.0	11.0	43	20
1,2-Dichloroethene	3.2	6.9	8.0	42	15
Chloroform	40	76	89	37	16
1,2-Dichloroethane	160	230	250	22	8.3

[a]The precision results include both sampling and analytical precision because the samples are not exact replicates. The canisters were filled sequentially from the vapor line.

[b]RSD = relative standard deviation.

[c]RPD = relative percent difference between No. 2 and No. 3.

TABLE E-34. ACCURACY RESULTS FOR METALS

Metal	Units	Measured Concentration (unspiked sample)	+	Spike Concentration	=	Total	Measured in Spiked Sample	Spike Recovery (Percent)
Copper	mg/L	0.42		0.40		.82	.53	65
Nickel	mg/L	<0.03		0.10		.10	.08	80
Zinc	mg/L	0.01		0.10		.11	.08	70
Chromium	mg/L	<0.03		0.20		.20	.22	110

TABLE E-35. PRECISION RESULTS FOR METALS (ppm)

Metals	No. 1	No. 2	No. 3	% RSD
Arsenic	.041	.032	.058	30
Cadmium	<.01	<.01	<.01	0
Chromium	.12	.11	.11	5.1
Copper	30	31	31	1.9
Lead	<.005	<.005	<.005	0
Mercury	.006	.008	.006	17
Nickel	.51	.50	.58	8.2
Selenium	<.005	<.005	<.005	0
Zinc	.28	.33	.29	8.8
Antimony	<.2	.32	<.2	29
Berylium	<.01	<.01	<.01	0

TABLE E-36. PRECISION RESULTS FOR SOLIDS (g/L)

	Dissolved Solids	Filterable Solids
No. 1	14	1.3
No. 2	14	1.4
No. 3	14	1.4
% RSD	0.0	4.2

QUALITY ASSURANCE FOR PLANT G

The general QA/QC project plan is presented in Quality Assurance Plan: Hazardous Waste Pretreatment for Emissions Control, RTI, 1984, and the site-specific plan is described in Site Specific Test and QA Project Plan Addendum Hazardous Waste Pretreatment for Emissions Control: Field Evaluation Plant G, RTI, 1985. The analytical work was performed by Industrial Environmental Analysts, Inc. (IEA). The program's data quality objectives are given in Table E-37.

GC and GC/MS Analyses

A standard mixture of VOC in nitrogen is prepared in a large glass container. A sample of the standard gaseous mixture is withdrawn periodically to serve as the control for the GC headspace analyses. The gas sample from the standard is analyzed in an identical manner to the gas sample withdrawn from the headspace.

Liquid samples are analyzed by gas chromatography using flame ionization detectors. The liquid samples were extracted with methylene chloride, and the methylene chloride injected into the chromatograph.

GC/MC was used in a qualitative mode to verify the components identified by retention time by the gas chromatography. All reported compounds were verified by GC/MS.

Data Assessment

For each major measurement parameter, the completeness, precision, and accuracy of the measured data were evaluated. Completeness is a measure of the number of acceptable samples or data points actually obtained, divided by the number that were planned. Ways in which a sample can become "incomplete" or voided include not collecting the sample, sampling incorrectly, losing or breaking the sample in shipment, improper sample preservation, consuming the whole sample in a voided analysis, or outlier data point rejection. The completeness of the field tests was 93 percent.

After the field sampling at Plant G, an audit sample was provided to IEA by the RTI QA officer. The sample consisted of several organics and was analyzed neat by GC/FID. The results were an average of 30 percent higher than the known concentrations (Table E-38). This exceeds the bias objective for the project (25 percent) and indicates the reported concentrations of the analyzed samples are probably higher than the actual concentrations.

Duplicate Analyses

Duplicate analyses were not performed on the collected samples because of sample size limitations. Because multiple samples were taken from sampled process streams, with the process operating at steady state, the variations within these multiple samples are composed of both the analytical variations

TABLE E-37. PRECISION, ACCURACY, AND COMPLETENESS OBJECTIVES

Parameter	Units	Method	Precision (% RSD)	Accuracy (% bias)[a]	Completeness[b] (%)
Waste material flow rate	g/s	Mass flowmeter or calibrated container	10	10	100
Source dimensions	cm	Ruler	5	3	100
Gas temperature	°C	Thermometer	5	1	100
Liquid temperature	°C	Thermometer	5	1	100
Waste volume	m^3	Dip stick	5	2	100
Gas flow rate	m^3/s	Calculated	10	10	100
pH of liquid	pH	EPA 150.1	±.1 units	±.1 units	100
Liquid density	g/m^3	Gravimetric	1	1	100
Solids content of liquids	percent	209 C, D, E,[c] H as applicable	10	10	100
Water content of liquids	percent	ASTM, D-1744	20	10	100
Volatile organic compounds in vent gas	g/m^3	Evacuated canister/ GC-FID	25	25	100
Volatile organic compounds in liquid samples	mg/L	GC-FID headspace GC-TCD direct analysis GC-MS	25 25 Qual.	25 25 Qual.	100 100 100

[a]Percent bias = $\frac{\text{observed - expected}}{\text{expected}} \times 100\%$.

[b]The number of valid data points divided by the number of planned data points expressed as a percentage.
[c]Standard Methods for the Examination of Water and Wastewater, 15th. ed.

TABLE E-38. QA SAMPLE ANALYSIS

Compound	Actual volume (ppm)	Concentration (μg/mL)	Measured concentration (μg/mL)	% Error
Nitrobenzene[a]	30.0	36.1	48.7	34.9
2-Nitrotoluene[a]	1.0	1.16	1.56	34.5
4-Nitrotoluene[b]		5.59	6.73	20.4
Average % error				29.9

[a]Sample prepared by volume ppm.
[b]Sample prepared by weight.

and any concentration changes occurring within the sampled streams. Table E-39 shows the high value, low value, mean, standard deviation, and percent RSD for each of the concentrations measured.

Each of these RSDs exceeds the accuracy objectives (25 percent), but because the calculated RSD also includes actual concentration differences of the streams, the collected data are probably acceptable. It is impossible to determine how much of the observed deviation was due to actual concentration changes or to analytical variation because no duplicate analyses were performed on an individual sample.

The very high RSDs for the toluene and 1,5-hexadiyne result primarily from concentration variations in the vent gas, which was confirmed by total hydrocarbon analysis onsite.

Spiked Samples

Liquid sample FCC-1-VOC-3A was spiked with known concentrations of nitrobenzene, 2-nitrotoluene, and 4-nitrotoluene, then analyzed in the same manner as the samples. The recovery of the spikes was 142 percent for nitrobenzene, 99 percent for 2-nitrotoluene, and 124 percent for 4-nitrotoluene. These data indicate that the analytical data produced by this field trip can be considered only marginally acceptable.

TABLE E-39. CONCENTRATION VARIATION WITHIN SAMPLED STREAMS

Sample stream	Nitrobenzene (μg/mL) High	Low	Mean	SD	%RSD
Feed F1	620	380	505	133	26
Aqueous effluent B1	66	28	41	19	46
Carbon effluent B2	4.3	<0.8	<0.8	--	--
Organic condensate 0	890,000	760,000	787,000	93,000	12
Aqueous condensate C	2,700	1,430	1,900	696	37
Vent gas V	<0.015	<0.015	<0.015	--	--
Average % RSD					30

	2-Nitrotoluene (μg/mL) High	Low	Mean	SD	%RSD
Feed F1	110	54	78	28	36
Aqueous effluent B1	4.6	0.9	2.4	1.6	67
Carbon effluent B2	<0.8	<0.8	<0.8	--	--
Organic condensate 0	220,000	170,000	193,000	25,000	13
Aqueous condensate C	110	42	87	39	45
Vent gas V	<0.015	<0.015	<0.015	--	--
Average % RSD					40

	4-Nitrotoluene (μg/mL) High	Low	Mean	SD	%RSD
Feed F1	68	42	51	12	24
Aqueous effluent B1	5.6	4.0	4.4	0.9	21
Carbon effluent B2	<0.8	<0.8	<0.8	--	--
Organic condensate 0	110,000	70,000	97,000	23,000	24
Aqueous condensate C	57	23	45	19	42
Vent gas V	<0.015	<0.015	<0.015	--	--
Average % RSD					28

	Toluene (μg/mL) High	Low	Mean	SD	%RSD
Feed F1	--	--	--	--	--
Aqueous effluent B1	--	--	--	--	--
Carbon effluent B2	--	--	--	--	--
Organic condensate 0	--	--	--	--	--
Aqueous condensate C	--	--	--	--	--
Vent gas V	1.4	0.077	0.413	0.559	135

	1,5 Hexadiyne (μg/mL) High	Low	Mean	SD	%RSD
Feed F1	--	--	--	--	--
Aqueous effluent B1	--	--	--	--	--
Carbon effluent B2	--	--	--	--	--
Organic condensate 0	--	--	--	--	--
Aqueous condensate C	--	--	--	--	--
Vent gas V	5.5	0.12	1.4	2.3	164